

ST. LAWRENCE RIVER SEDIMENT
AND
BIOLOGICAL ASSESSMENT
1991

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ST. LAWRENCE RIVER SEDIMENT AND BIOLOGICAL ASSESSMENT, 1991

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EXECUTIVE SUMMARY

Cornwall, Ontario and Massena, New York are major industrial centres on the St. Lawrence River. Previous surveys have identified municipal and industrial discharges on both sides of the river which contribute contaminants such as mercury, zinc, phosphorus, PCBs and phenols. The pollution in this river is a concern since the St. Lawrence River is an important water resource.

Water, sediment and benthic samples were collected from 17 stations in the St. Lawrence River near Cornwall, Ontario in March, 1991. Sediment was collected from eight of the seventeen stations for sediment bioassays using mayfly nymphs, *Chironomus* larvae and juvenile fathead minnows. The main focus of this study was to assess the sediment as a source of mercury to biota. Benthic macroinvertebrates were collected for total mercury analysis. A correlation between the concentration of mercury in benthos and sediment mercury concentration may be an indication of mercury availability from the sediment. Sediment and water were also analyzed for a variety of other metals, nutrients and physical parameters since metal contamination in general is a concern. This study also serves as an update to the 1985 sediment and water quality survey (Anderson 1990).

Water contaminant concentrations at stations in the St. Lawrence River were compared with the Provincial Water Quality Objectives (Ontario Ministry of the Environment 1984). The objectives were not exceeded at any sampling stations. For many contaminants, concentrations were below the method detection limit. The only metal that increased in water downstream of the reference stations was zinc. The highest mean concentration was observed at station 368 (0.012 mg/L) downstream of Courtauld's Fibre's shore-based outfalls which were known to be a source of zinc. Zinc concentrations remained significantly higher (Tukey's Studentized Range Test $p < 0.05$) downstream of the shorebased outfalls and Courtauld's open water diffuser than at any of the upstream stations. Courtauld's was the largest aquatic discharger of zinc in the Province of Ontario prior to its closure in November, 1992 (OMOE, 1992a).

In general, the majority of sediment samples collected from the Cornwall/Massena area of the St. Lawrence River have contaminant concentrations greater than the Provincial Sediment Quality Guidelines "lowest effect level" (LEL). Although not investigated in this study, there may be an impact on the benthic community. Review of the particle size corrected data suggest that there are no significant local point sources of cadmium, chromium, nickel, arsenic, iron, aluminum and manganese. The concentration of these contaminants in Cornwall reflect upstream loadings from Lake

Ontario. Sediment concentrations of mercury, lead, copper and zinc were above the "Severe Effect Level" (SEL) at station 368. This station is downstream of Courtaulds Fibre's shore based outfalls. The high concentration of these contaminants in their effluent relative to other sources in the area (with the exception of copper), suggest that Courtaulds Fibres was an important source of these contaminants to the St. Lawrence River.

A qualitative comparison between data from 1991 and 1985 shows that contaminant concentrations have increased at some stations and decreased at others without a consistent pattern. The only exceptions are stations 369, 371 and 374 where increases in contaminant concentrations in 1991 were seen for all contaminants analyzed. The changes in contaminant concentrations observed were likely due to sample differences in percent fine particles rather than changes in local or upstream contaminant loadings. Overall, the percentage of stations with contaminant concentrations above the LEL for biotic impact is similar between 1991 and 1985.

There are several point and non point sources of mercury in the Cornwall area. Concentrations of total mercury in the sediment were significantly higher at several stations downstream of the point sources when compared to upstream reference stations. Several stations had sediment concentrations above the SEL. Concentrations decreased with increasing distance from the point sources. Sediment methyl mercury concentrations remained high downstream of mercury point sources when compared with upstream reference sites and then gradually decreased as the distance from the sources increased.

The tissue concentrations of mercury in benthos appear to be influenced by their proximity to the anthropogenic source of mercury. Benthos collected from station 368 downstream of the Courtaulds shore based outfalls and station 368A about 50 metres downstream of the diffuser had significantly higher mercury tissue concentrations than benthos collected from other sites. Mercury in benthos was significantly correlated with mercury and methyl mercury concentrations in sediment, however, the correlations were weak.

Concentrations of mercury in benthos collected downstream of station 368 and 368A were lower than expected based on sediment mercury concentrations. Despite similar concentrations of methyl mercury and concentrations of total mercury above the SEL, benthos did not accumulate high concentrations of mercury. Other factors such as TOC may have influenced mercury uptake by biota by affecting mercury bioavailability.

The bioassay results show that the sediment at station 368 is marginally toxic to *Chironomus tentans* larvae. The sediment from station 368 and 368A consistently elicited a sublethal response to both *Hexagenia limbata* and *Chironomus tentans* and station 369 caused sublethal responses to *Chironomus tentans*. In addition, tissue

concentrations of lead, copper, zinc and mercury were higher in minnows exposed to sediment from station 368 than concentrations found in minnows exposed to other sediment. Sediment concentrations of these four metals were above the SEL at this station. Sediment mercury concentrations were also greater than the SEL at station 368A and 369. This is strong conclusive evidence that sediment contamination has a potential to impair native species particularly at station 368 and possibly at station 368A and 369. The results of the sediment bioassay are consistent with the field survey.

The high total mercury concentrations in sediment at all stations downstream of the local point sources when compared with upstream reference sites suggests an impact on environmental conditions in the St. Lawrence River. The presence of higher concentrations of methyl mercury downstream of sources compared with upstream reference sites suggests the potential for continued contamination of the food chain. Studies in Lake St. Francis downstream of Cornwall (Sloterdijk 1991) show higher mercury concentrations in sediment when compared with Lake St. Lawrence reference sites, the source of which has been attributed to Cornwall. Sport fish in the north channel and Lake St. Francis have been contaminated with mercury since the 1970s when testing for mercury first began in the area (Ontario Ministry of Environment, Ontario Ministry of Natural Resources 1992). Some of the contaminated sediment close to the sources are likely in a state of flux and are flushed downstream where they contribute to the mercury loading in Lake St. Francis making the mercury bioavailable at least temporarily before being carried further downstream (Sloterdijk 1991, Lorrain, personal communication).

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INTRODUCTION

The St. Lawrence River is a major international waterway. It is the outlet of the Great Lakes, and had a drainage basin of 1,184,324 km² (Germain and Jenson 1984). Most of the water entering the river from Lake Ontario originates from the other four Great Lakes and interconnecting channels and, therefore, reflects contaminant loadings from numerous sources within the basin. The potential for contaminant transfer from the Great Lakes to the St. Lawrence is great, however; the existence of point and non-point sources to the river is also of concern.

Cornwall, Ontario and Massena, New York are major industrial centres on the St. Lawrence River. Previous surveys have identified municipal and industrial discharges on both sides of the river which contribute contaminants such as mercury, zinc, phosphorus, PCBs and phenols. The St. Lawrence River at Cornwall/Massena has been designated an Area of Concern by the Great Lakes Water Quality Board of the International Joint Commission. As such, a Remedial Action Plan (RAP) to clean up the contaminants is being developed. The boundaries of the RAP extend from Maitland, Ontario downstream through Lake St. Francis.

The pollution in this river is a concern since the St. Lawrence River is an important water resource; the river and lakes downstream are used for a variety of purposes including recreational and commercial fishing and hunting and serves as a source of drinking water for some communities in Ontario and Quebec. The Mohawk community of Akwesasne has historically relied on the river for fish and wildlife. Commercial fish and sport fish (specifically walleye, pike and smallmouth bass) in the Cornwall area have been limited or restricted for human consumption because of mercury contamination since 1970 when testing for mercury first began in the area.

Local point sources at the time of the survey (March, 1991), on the Canadian side of the river included ICI Forest Products (a mercury cell chlor-alkali plant), Cornwall Chemicals (producers of sodium hydrosulphide, hydrochloric acid, carbon tetrachloride and carbon disulphide), Courtaulds Fibres (a rayon manufacturer), Domtar Fine Paper LTD. (pulp and paper mill) and the municipal sewage treatment plant (STP). In November, 1992 Courtaulds Fibres closed its' operation in Cornwall, Ontario. This closure will result in the elimination of a significant source of contaminants. Non-point sources to the river include agricultural run off, storm sewers, combined sewer overflows and atmospheric deposition.

Sediment, water and benthic samples were collected from 17 stations. The main focus of this study was to assess the sediment as a source of mercury to biota. Accordingly, we measured total mercury and methyl mercury in the sediment. Methyl

mercury was analyzed since it is the most available form of mercury to the biota. Benthic macroinvertebrates were collected for total mercury analysis. A correlation between the concentration of mercury in benthos and sediment mercury concentration may be an indication of mercury availability from the sediment. Sediment and water were also analyzed for a variety of other metals, nutrients and physical parameters since metal contamination in general is a concern. This study also serves as an update to the 1985 sediment and water quality survey (Anderson 1990).

Because of the tremendous flow in the St. Lawrence River and its dilution capacity, the concentrations of inorganic contaminants in the water tend to be low. Mercury concentrations in the water of the St. Lawrence River in 1989 ranged from 0.4 to 0.9 ng/L (ppb) (MOE unpublished data) which is typical of uncontaminated freshwater and marine systems (Fitzgerald 1979). The sediment, however, has historically been contaminated with mercury (Kauss *et al.* 1988) and although concentrations have decreased since 1975 they still remain high (Anderson 1990). At present, the importance of the contaminated sediment as a source of mercury to the biota relative to the continual input from point sources is unknown.

METHODS

Sediment, water and benthos from the Cornwall region of the St. Lawrence River were collected in March, 1991. Site selection was based on the location of open water discharges (Domtar Fine Papers/ICI Forest Products/Cornwall Chemicals, Courtaulds Fibres and the STP) and shore-based discharges (Courtaulds Fibres) and results from sediment surveys in 1979 and 1985 (Kauss *et al.* 1988; Anderson, 1990). Two sites (station 82 and 83) were selected in Lake St. Lawrence as upstream reference sites (Figure 1 & 2 Table A1).

Water Collection for Contaminant Analysis

Water samples were collected at one metre depth from 17 stations using a March submersible pump. To minimize contaminant transfer among stations the teflon tubing was cleaned between stations with dilute acid then rinsed with distilled water and flushed with river water. Three successive samples were collected from each station. A sample blank (distilled water passed through the tubing) was collected at every fourth station. There were four sample blanks in total. All samples were acidified at the time of collection and kept refrigerated until delivery to the MO Rexdale laboratory. Delivery was within one week of collection. Water samples were analyzed for conductivity, DOC, metals and nutrients (Table 1).

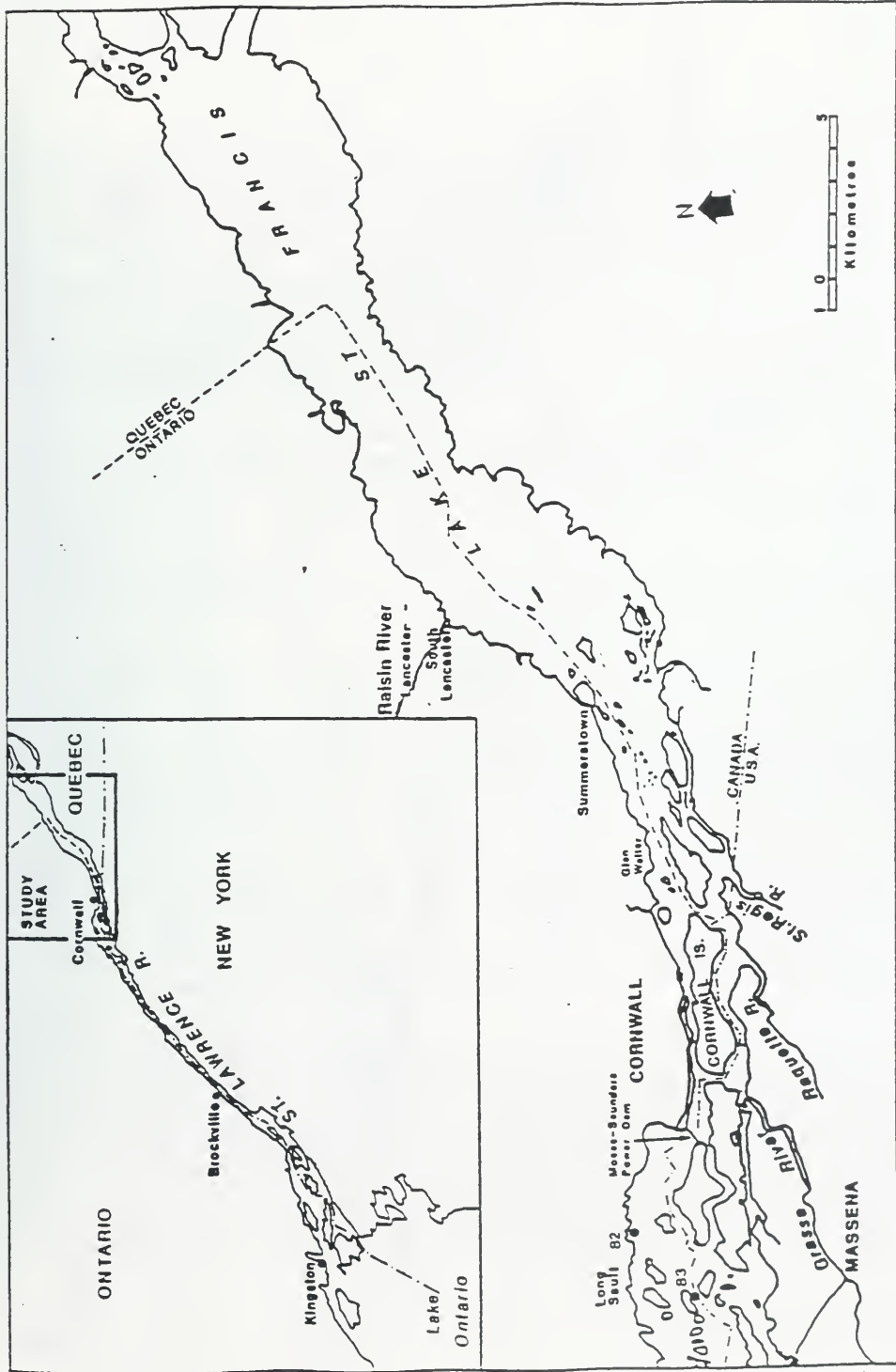


FIGURE 1

SAMPLING LOCATION

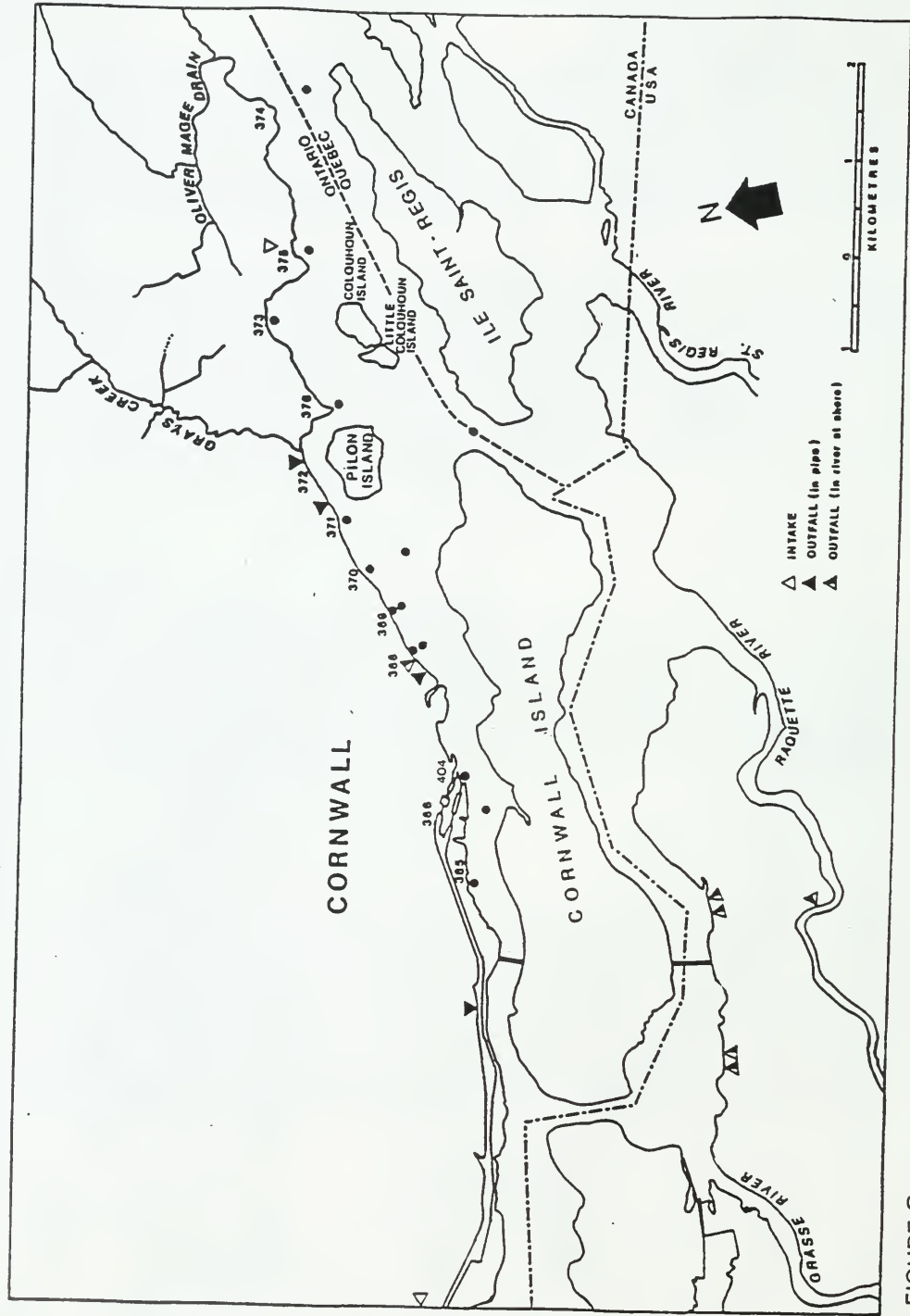


FIGURE 2

Sampling Locations

Three samples from each of five stations were collected at one metre depth using a Master Flex peristaltic pump fitted with teflon tubing following "ultra clean" sampling techniques described by Mierle (personal communication) and analyzed for mercury at the MOEE Dorset Research Centre following the procedure by Mierle (1990).

Measurement of Water Temperature and Conductivity

Water temperature and conductivity were measured at the time of water collection using a Lise/Metric conductivity meter calibrated daily.

Table 1: Sediment and water samples were analyzed for the following parameters.	
Total Organic Carbon Phosphorus Total Kjeldahl Nitrogen	
Selenium Chromium Mercury Arsenic Lead Aluminum	Cadmium Manganese Zinc Nickel Iron Copper
Sediment samples only; Methyl mercury Loss on Ignition Particle Size	

Sediment and Live Benthic Macroinvertebrate Collection for Contaminant Analysis

Sediment

Sediment was collected with a stainless steel Ponar grab from 17 stations. A portion of the upper three centimetres of at least five grab collections were pooled and homogenized for each sample. The remainder of the sample was sieved for benthos. This format was continued until sufficient sediment and benthos were collected to fulfil the weight requirements for each sample. Since many grabs were needed to obtain one gram of benthos, the portion of sediment taken from the grab sample for the chemical analysis was small to ensure that the sediment sample, in its entirety, was representative of all grabs needed for benthos collection.

Three samples were collected at nine of the 17 stations. At five of these nine stations, enough sediment was collected so that one of the samples could be homogenized and then split into two sample containers to evaluate laboratory analytical precision. Two successive samples were collected at the remaining eight stations. Sediment samples were analyzed for a variety of chemical and physical parameters (Table 1). One gram of each of the homogenized samples was placed in teflon coated containers specific for total and methyl mercury analysis.

Sediment samples were kept on ice in the field, and subsequently were refrigerated at 4°C in the dark until analysis. The general sample composition (e.g. sand, silt etc.), sediment colour, any unusual features and the number of grabs required for the composite was recorded (Table A2).

On Board Measurement of pH and Eh

Sediment pH and Eh were measured at the time of collection with a portable Radiometer PMH 80 meter.

Live Benthic Macroinvertebrates Collection

Macroinvertebrates (chironomids and oligochaetes) were collected for mercury analysis. At each of the 17 stations the sediment sectioned for benthic macroinvertebrate collection was sieved through a 500 μm mesh. A plastic sieve was used to minimize contamination of the samples. Materials retained on the sieve were manually sorted and then benthic macroinvertebrates were separated into families.

One gram (wet weight) of organisms from the same family (to reduce variability), was placed in acid washed, hexane-rinsed glass jars containing a three centimetre depth of sediment (top three centimetre subsection). The remainder of the jar volume contained site water. Three samples were collected from each station following this procedure. Jars were held unsealed and on ice in the field. Live organisms were held at ambient sediment temperature, with gentle aeration, for no more than 24 hours prior to sample preparation.

At five stations, two grams of organisms were collected and then placed into two jars to test laboratory precision.

Several litres of site water were collected in the field for use in sample preparation.

Sample Preparation of Live Benthic Macroinvertebrates

Within 24 hours of collection, macroinvertebrates were removed from their holding vessels by sieving the sediments through 500 μm mesh. Chironomid larvae were placed in acid-washed, hexane-rinsed glass beakers containing 500 ml of site water.

Oligochaetes were placed in beakers containing 500 ml of site water and three centimetre of sediment from an uncontaminated site chosen upstream of all sources.

Water was changed three times over the course of 24 hours to prevent coprophagy. After gut clearance, organisms were patted dry and placed in clean five millilitre conical teflon vials and were immediately frozen. Oligochaetes were removed from the beakers by sieving and then placed in the vials.

Frozen macroinvertebrates were delivered on dry ice to the MOEE Dorset laboratory within one week of collection.

Sediment Bioassays

Sediment was collected with a stainless steel ponar grab from station 82, 83, 368, 368A, 369, 370, 374 and 375 for bioassays to estimate acute and chronic toxic effects associated with the sediment and the presence or absence of bioavailable mercury for uptake by "clean" laboratory biota. Mortality and growth inhibition in mayfly nymphs, *Chironomus* larvae and juvenile fathead minnows were used as indicators of toxicity.

Sediment bioassay tests followed the OMOEE standardized procedures (Bedard *et al.* 1992). The bioassays were static, single species tests using whole sediment. The test chambers were 1.8 litre containers, prepared sediment and dechlorinated tap water (1:4, V:V). Detailed test procedures are provided in Bedard and Petro (1992). Briefly, ten mayfly nymphs or 15 second instar chironomid larvae were added to triplicate jars for each test and control sediment for 21 or 10 days respectively. Mortality and growth (changes in weight) were recorded to determine acute and chronic toxic effects. Juvenile fathead minnows were exposed to each test and control sediment for 21 days.

Contaminant Analysis of Sediment and Water

All laboratory analytical procedures for contaminants in sediment and water (with the exception of mercury in sediment and the water samples sent to Dorset (Mierle 1990) followed the methodology outlined in the Handbook of Analytical Methods for Environmental Samples (MOE 1983). The procedure for mercury analysis in benthic tissue is described in Rasmussen *et al.* (1991).

Total and methyl mercury analysis on sediment samples was by contract laboratory (Brooks Rand LTD, Seattle Washington). Analytical procedures for sample digestion are described in Bloom and Crecelius (1987). Samples for inorganic mercury analysis were digested in 5 ml of 7:3 HNO₃/H₂SO₄ at 70 °C for three hours and samples for methyl mercury analysis were digested with 10 mL of 25% KOH in methanol (Bloom

1989). After digestion samples were diluted and small aliquots, following the procedures of Fitzgerald and Gill, (1979) and Bloom and Fitzgerald, (1989) were analyzed for total mercury using cold vapour atomic fluorescence spectrometer (CVAFS). Methyl mercury analysis of digestate followed the procedure of Bloom, (1989). Digestates were placed into a bubbler with deionized water, buffered to pH 4.9 and ethylated with 1% sodium tetraethylborate for 20 minutes. The samples were purged with nitrogen for 25 minutes at 250 ml/min onto graphitized carbon traps which retain the organomercury species. The carbon trap was further dried and the organomercurials were thermally desorbed into a 45 cm GC column. The column will trap the volatile compounds which will then pass through a thermal decomposition tube prior to detection of the release Hg^0 by CVAFS.

Data Analysis

All sediment, water and benthic tissue data were log transformed using natural logarithms prior to statistical analysis to satisfy assumptions of normality.

Mean inorganic contaminant concentrations in sediment and water were compared among stations using a one way ANOVA. The Tukey's Studentized Range Test was applied to test station differences and to determine if contaminant concentrations in sediment, benthos and water at each station were significantly different from the upstream reference stations in Lake St. Lawrence. Higher contaminant concentrations in sediment, water and benthos in the Cornwall area when compared with the upstream reference sites would suggest local contaminant sources.

The Pearson product-moment correlation was performed using the SAS statistical package (SAS Institute Inc. 1988) to examine the relationship between sediment contaminant concentrations and physical parameters of the sediment. A principal components analysis using the Numerical Taxonomy and Multivariate Analysis System (NTSYS-pc; Rohlf 1988) was also used to reduce the data into three components representing the variables that best correlate with one another and explain the major sources of variation in sediment quality among the 17 stations.

Using the SAS discriminant analysis procedure, the Pearson's Product Moment total-sample correlation coefficients and the between-class correlation coefficients were estimated. The total-sample correlation coefficient uses all the values for each parameter and ignores station effects to determine the relationship between parameters, whereas the between-class correlation analysis estimates the relationship between parameters across stations by using the mean values at each station. This comparison will indicate if parameters are behaving the same way at all stations.

Trace elements tend to accumulate and bind to the clay/silt sediment fraction represented by particle sizes of less than $62\ \mu\text{m}$ (Forstner and Wittmann 1979;

Krumgalz *et al.* 1992). The heterogenous nature of the sediment in the St. Lawrence River makes it necessary to adjust trace element concentrations for the different particle size distributions at the various sampling stations in order to compare contaminant concentrations between stations and identify trace metal contaminant sources. To correct for particle size differences between stations a regression analysis was performed on log transformed trace metal concentrations and the percentage clay plus silt fraction. This fraction was chosen since the Pearson correlation matrix showed that the silt/clay fraction had the highest correlation (correlation coefficient ranged from 0.7824 to 0.9117) with sediment metal concentrations, as compared with the sand, silt or clay fraction individually (although correlation coefficients were high for all these fractions). The mean residuals for each station derived from the regression analyses were then statistically compared to determine if there were significant differences between stations using a one way Analysis of Variance and Tukey's Studentized Range Test. The regression analysis is expected to explain or account for the variability due to particle size while the residual data represents the variability attributable to other factors such as the presence of local point sources. Differences between mean residual values may suggest the presence of a point source.

RESULTS and DISCUSSION

Water Quality

Metal Concentrations in Water

Water quality data are provided in Table A3. Water contaminant concentrations at stations in the St. Lawrence River were compared with the Provincial Water Quality Objectives (Ontario Ministry of the Environment 1984). The objectives were not exceeded at any sampling stations. Arsenic, cadmium and lead were below the method detection limit (i.e. MDL) at all stations (Table A3) and iron was below the analytical detection limit at all stations with the exception of station 365 and 373, and in one replicate sample at stations 368, 371 and 372. In all cases iron concentrations were low (range 0.03 to 0.1 µg/L).

All stations sampled had the same or similar concentrations of chromium (0.001 mg/L), manganese (0.002 mg/L), copper (0.001 mg/L) and nickel (0.003 mg/L) with the exception of a few stations where copper and nickel were below the method detection limits.

The only metal that increased in water downstream of the reference stations was zinc (Figure 3). Concentrations of zinc in water at stations ranged from below the method detection limits to 0.012 mg/L. The highest mean concentration was observed at station 368 (0.012 mg/L) downstream of Courtauld's shore-based outfalls which were known to be a source of zinc. Zinc concentrations remained significantly higher (Tukey's Studentized Range Test $p < 0.05$) downstream of the shorebased outfalls and Courtauld's open water diffuser than at the upstream stations. Courtauld's was the largest aquatic discharger of zinc in the Province of Ontario (OMOE, 1992a).

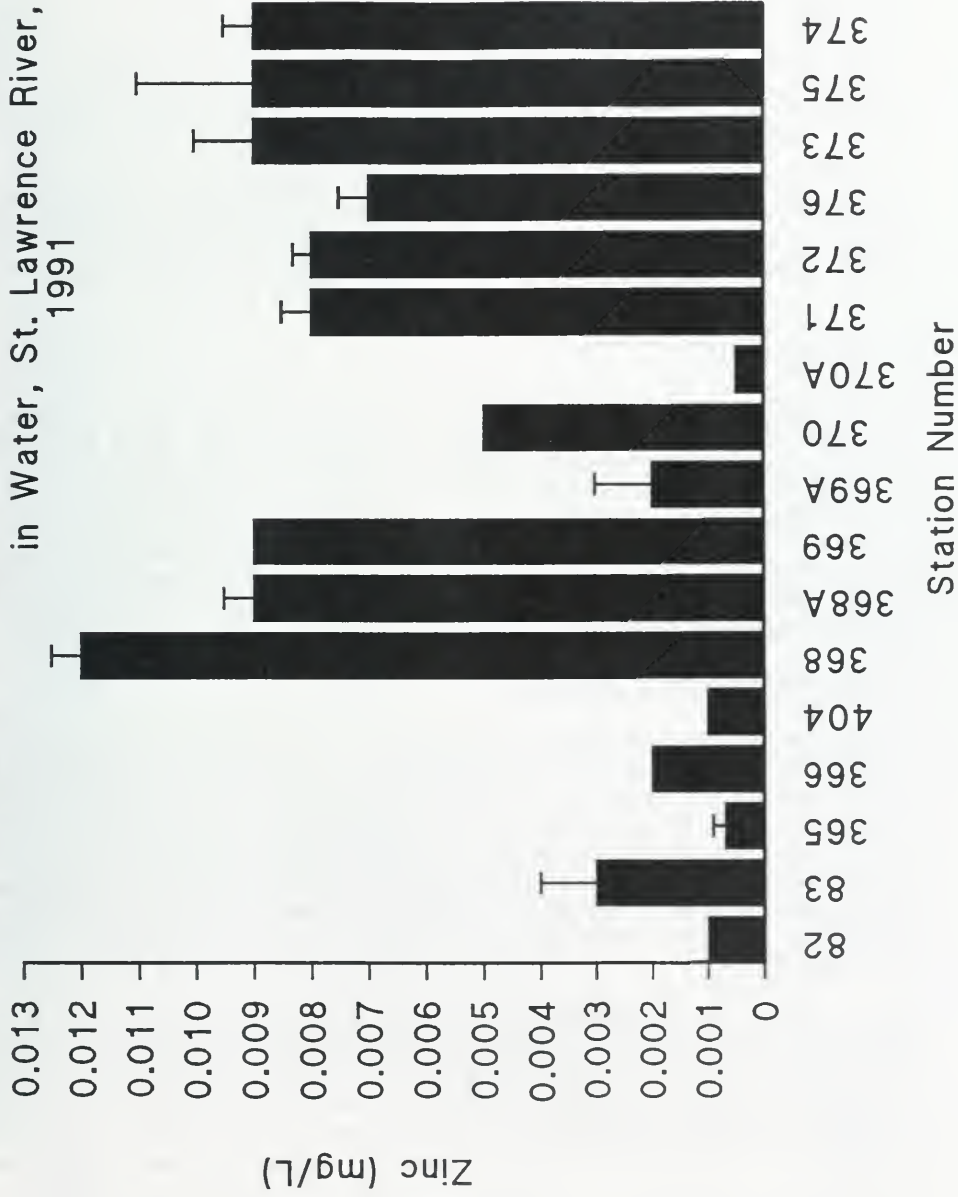
Mercury concentrations were below the traditional method detection limit (0.02 µg/L) in all cases for samples analyzed by the MOEE Rexdale laboratory. Water samples analyzed at the MOEE Dorset laboratory showed that concentrations ranged from 2 to 3.5 ng/L. These concentrations are higher than concentrations reported in 1989 which ranged from 0.3 to 0.9 ng/L (OMOE unpublished data). It is not known if the higher concentrations represent sample contamination or actual increases in mercury concentrations in the water. Unlike the samples collected for this survey, previous samples were collected in the summer. Seasonal trends in mercury have been observed (Jackson *et al.* 1982; Jackson 1986; Parks *et al.* 1986; Parks *et al.* 1989) and may be the cause of the higher concentrations relative to 1989.

The concentration of all metals (with the exception of chromium and zinc) were below the method detection limits in the four blank samples. Chromium concentrations in the blanks were the same as in all other water samples (0.001 mg/L). Concentrations of zinc ranged from non detectable to 0.002 mg/L (Table A3).

Nutrient Concentrations in Water

Mean total phosphorus concentrations in water were low (generally less than 12 µg/L), with the exception of one of the reference stations (station 82) and station 373 where mean concentrations were 35 µg/L [Standard Deviation; SD 31 µg/L] and 28 µg/L [SD 4 µg/L] respectively (Table A4). Phosphorus concentrations at station 373 were significantly higher than concentrations at the other stations (Tukey's Studentized Range Test $p < 0.05$). Nuisance algal growth is unlikely in rivers and streams if concentrations of total phosphorus remain below 30 µg/L during the ice-free season (Ontario Ministry of Environment, 1984). Water samples were collected in winter and are not representative of summer conditions; however, past summer surveys (Kauss *et al.* 1988; Anderson and Biberhofer 1991) have shown that concentrations tend to be below this guideline in the St. Lawrence River. Total phosphorus concentrations were similar to concentrations in water samples collected in the winter at Wolf Island from 1977 to 1983 (Sylvestre *et al.* 1987).

Figure 3. Mean (\pm SD) Zinc Concentration (mg/L)
in Water, St. Lawrence River,
1991



Mean total kjeldahl nitrogen concentrations were similar to past surveys and were not high (range 210 to 360 $\mu\text{g/L}$; Sylvestre *et al.* 1987; Kauss *et al.* 1988; Anderson and Biberhofer 1991, Pope 1993). Mean alkalinity ranged from 98 to 100 mg/L and was typical for the St. Lawrence River (Sylvestre *et al.* 1987; Anderson and Biberhofer 1991). Dissolved organic carbon concentrations ranged from 1.9 to 2.6 mg/L similar to concentrations found previously at Wolf Island and other upstream stations in the St. Lawrence River (Pope 1993).

Water samples collected as blanks had phosphorus concentrations which ranged from below the MDL to the MDL (0.002 mg/L). TKN concentrations ranged from 0.07 to 0.100 mg/L, well below concentrations detected in the river water samples. These results suggest minimal sample contamination from sample handling (Table A4).

Sediment Quality

Sediment contaminant concentrations were compared with the Provincial Sediment Quality Guidelines (Persaud *et al.*, 1992; Tables 2 and 3 and Tables A5 and A6). These guidelines describe three "effect" levels for different contaminants in terms of potential effects on the benthic community: (1) the no observed effect level; (2) the lowest effect level (LEL) which is the level of sediment contamination that can be tolerated by the majority of benthic organisms. Concentrations greater than this level indicate that the benthic communities in these areas may be impaired; and (3) the severe effect level (SEL). This is the sediment concentration of a compound that is expected to be detrimental to the majority of benthic species.

Metal Concentrations in Sediment.

Within the area of study, concentrations of mercury, zinc, lead, copper, chromium, nickel, arsenic, cadmium and iron in sediment were all greater than the LEL at many sampling stations. The LEL was exceeded in 13% of the sediment samples analyzed for arsenic, 83% analyzed for cadmium, 52% of the chromium samples, and 73% of the samples analyzed for copper. In the case of iron, many of the sediment samples approached the LEL but only six percent exceeded it. Sixty-nine percent of the mercury samples exceeded the LEL and 15% exceeded the SEL. The percentage of sediment samples exceeding the LEL for nickel, lead and zinc were 63%, 52% and 52% respectively.

Zinc, lead and mercury concentrations in sediment were above the SEL at the site located just below the Courtaulds Fibre shore-based discharges (station 368). Mean concentrations were 1233 [SD 57.7] $\mu\text{g/g}$, 428 [SD 84] $\mu\text{g/g}$ and 3.13 [SD 0.15] $\mu\text{g/g}$ respectively. Copper concentrations equalled the SEL (mean 106 [SD 7.2] $\mu\text{g/g}$). This is the only station where the SEL was exceeded or attained for these metals with the exception of mercury which exceeded the SEL at several sites downstream of the

Table 2: Mean [Standard Deviation] Concentration of Metals in Sediment Collected From the St. Lawrence River, 1991.

Station Number	N	Aluminum μg/g	Arsenic μg/g	Cadmium μg/g	Chromium μg/g	Copper μg/g	Iron %	Manganese μg/g	Nickel μg/g	Lead μg/g	Selenium μg/g	Zinc μg/g
82	3	10833.3 [764]	2.8 [0.2]	1.2 [0.08]	26 [1.0]	20.3 [0.6]	1.4	230 [10]	18.8 [1.4]	18.5 [0.5]	0.6 [0.04]	80.7 [2.1]
83	3	5833.3 [208]	1.8 [0.1]	0.8 [0.1]	14.7 [0.6]	10.3 [0.6]	0.9	183.3 [5.8]	12.3 [0.6]	12.3 [2.6]	0.3 [0.03]	50.7 [2.1]
365	2	10500 [707.1]	4.3 [0.07]	1.4 [0.07]	33 [4.2]	50 [2.8]	1.5	245 [7.1]	26 [2.8]	35.5 [0.7]	1.4 [0.07]	115.97 [1.1]
366	3	7116.7 [202.1]	1.7 [0.3]	0.6 [0.06]	17.2 [1.1]	14.2 [1.3]	1.1	246.7 [0.8]	12.8 [0.8]	13 [1]	0.5 [0.04]	48 [2.6]
404	3	5566.7 [251.7]	1.4 [0.06]	0.8 [0.04]	16 [1.0]	17 [1.7]	0.9	196.7 [5.8]	13.7 [0.6]	21.7 [3.2]	0.4 [0.02]	52.3 [7.2]
368	3	12166.7 [1040.8]	4 [0.3]	1.6 [0.03]	53.7 [1.1]	▲ 105.8 [7.2]	1.6	236.7 [5.8]	27 [1]	▲ 428.3 [84]	2.5 [0.4]	▲ 1233.3 [57.7]
368A	2	10950 [1484.9]	3.1 [0.4]	1.2 [0.2]	27.5 [4.9]	28.5 [3.5]	1.4	270 [14.1]	20 [2.8]	32.5 [6.4]	0.9 [0.09]	385 [63.6]
369	2	13000	4.2 [0.1]	1.6 [0.1]	35 [1.4]	41	1.6	265 [7.1]	24.5 [0.7]	44	1.5 [0.07]	375 [7.1]
369A	3	6883.3 [475.2]	1.8 [0.2]	0.9 [0.1]	19.5 [1.3]	21.3 [2.1]	1.2	176.7 [5.8]	15.7 [1.1]	30.8 [5.1]	1.1 [0.06]	143.3 [15.3]
370	3	15000	5.4 [0.4]	1.6 [0.1]	36.3 [0.6]	43 [1.0]	1.6	320 [10.0]	28 [1.0]	36 [2.0]	2 [0.1]	616.7 [15.3]
370A	3	3866.7 [57.7]	0.9 [0.02]	0.5 [0.1]	12 [2.6]	10.2 [1.6]	0.7	146.7 [5.8]	10.7 [1.2]	10.7 [0.6]	0.4 [0.02]	65.3 [3.2]
371	2	16000	5.8 [0.5]	2.2 [0.07]	40	60 [1.4]	1.9	305 [7.1]	30	41	2.0 [0.07]	615 [7.1]
372	2	8750 [212.1]	1.9 [0.3]	0.8 [0.2]	20.5 [0.7]	17	1.3	240	16.5 [0.7]	13.5 [0.7]	0.7 [0.05]	60.5 [2.1]
376	2	15000	6.4 [0.2]	1.7	41.5 [0.7]	46.5 [0.7]	1.7	285 [7.1]	30.5 [0.7]	39.5 [0.7]	2.7 [0.1]	560
373	2	7500 [282.8]	1.2 [0.1]	0.5 [0.2]	16	8.7 [0.1]	1.0	165 [7.1]	11	8.9 [0.8]	0.3 [0.02]	75 [1.4]
375	3	19166.7 [763.8]	5.7 [0.3]	2.1 [0.06]	50.7 [1.5]	57.2 [1.9]	2.1	291.7 [2.9]	36	55.3 [5.7]	2.1 [0.1]	486.7 [20.8]
374	2	18500 [707.1]	6.8 [0.1]	2.0 [0.2]	47.5 [0.7]	51.5 [0.7]	2.1	295 [7.1]	36 [1.4]	49.5 [4.9]	2.6	405 [7.1]
Lowest Effect Level			6	0.6	26	16	2%	460	16	31		120
Severe Effect Level ▲			33	10	110	110	4%	1100	75	250		820

Table 3. Mean [Standard Deviation] Total Mercury and Methyl Mercury Concentrations in Sediment Collected From the St. Lawrence River, 1991.

Station Number	N	Total Mercury ($\mu\text{g/g}$)	Methyl Mercury ($\mu\text{g/g}$)
82	3	0.12 [0.01]	0.0013 [0.0004]
83	3	0.09 [0.004]	0.001 [0.0005]
365	2	♣ 3.26 [0.46]	0.0119 [0.001]
366	3	0.14 [0.02]	0.0021 [0.0009]
404	3	0.56 [0.03]	0.007 [0.001]
368	3	♣ 3.13 [0.15]	0.0075 [0.001]
368A	2	♣ 2.6 [0.45]	0.0084 [0.0008]
369	2	♣ 2.29 [0.16]	0.0091 [0.0028]
369A	3	0.98 [0.11]	0.0082 [0.0008]
370	3	0.19 [0.19]	0.0044 [0.0025]
370A	3	1.18 [0.13]	0.009 [0.0022]
371	2	1.1 [0.14]	0.0103 [0.0074]
372	2	0.16 [0.004]	0.0039 [0.0001]
376	2	1.18 [0.03]	0.0025 [0.0006]
373	2	0.06 [0.01]	0.00095 [0.00007]
375	3	1.16 [0.10]	0.002 [0.0008]
374	2	0.25 [0.05]	0.0026 [0.0022]
Lowest Effect Level		0.2	
Severe Effect Level ♣		2	

mercury sources. Concentrations of zinc, lead and copper were significantly higher at this site ($p < 0.001$) than at all the other sites sampled (Figure 4, 5 and 6). Concentrations of zinc and copper were also high at several stations downstream. In 1979 and 1985 this site also had high sediment metal concentrations (Kauss *et al.* 1988; Anderson 1990).

The percentage of fine particles at station 368 is high (81% [SD 1.25]) and the area has been described as a deposition zone (McQuest Marine Sciences LTD. 1991), therefore, it is not surprising to find high concentration of metals. However, the sediment contaminant concentrations may be enriched by the high concentrations of zinc and mercury present in Courtaulds' effluent at the shore based discharges (immediately upstream of station 368) and their open water diffuser 280 meters from the shore. There are no other upstream point sources of zinc or mercury that are of the magnitude of Courtaulds' effluent (OMOE 1992a and b). Fate and Transport modelling of zinc and mercury from local sources suggest that the shore based outfalls would have a large impact on contaminant loadings to this area (Nettleton 1994) and other downstream sites where both these metals are high. Based on this model, and based on river flow data which suggest that the area around station 368 is a deposition zone, Courtaulds Fibres may be the most important source of zinc and mercury to this site. Modelling results suggest that effluent from the open water diffuser will also impact downstream areas (Nettleton 1994).

Courtaulds has always discharged high concentrations of mercury and zinc (B. Helliard personal communication). The presence of these contaminants in the sediment may also be due to historical contamination in addition to the contribution from the recent discharges at the time of the survey. Furthermore, the discharge of mercury from the upstream chlor-alkali plant may also contribute to the mercury present at this site. Additional studies on sediment flux and stability will help determine the degree of sediment movement and deposition downstream.

Until recently Courtaulds discharged high concentrations of lead because of the corrosion of their lead pipes and their use of lead as a lining in their acid storage tanks. The high lead concentrations in the sediment downstream of the shore-based outfalls is likely a result of this historical contamination. Prior to its closure, the company had almost completely replaced its' lead pipes and tank lining with plastic products, however, during the survey the company still discharged higher lead concentrations than the other local upstream sources in the AOC (OMOE 1992a,b).

The source of the high concentrations of copper in the sediment can not be determined by reviewing the MISA effluent data. Similar loadings of copper were present in the effluent from both Courtaulds and Domtar Fine Paper LTD. located upstream of Courtaulds (OMOE 1992a and 1993).

Figure 4. Mean (\pm SD) Zinc Concentrations ($\mu\text{g/g}$)
in Sediment, St. Lawrence River,
1991

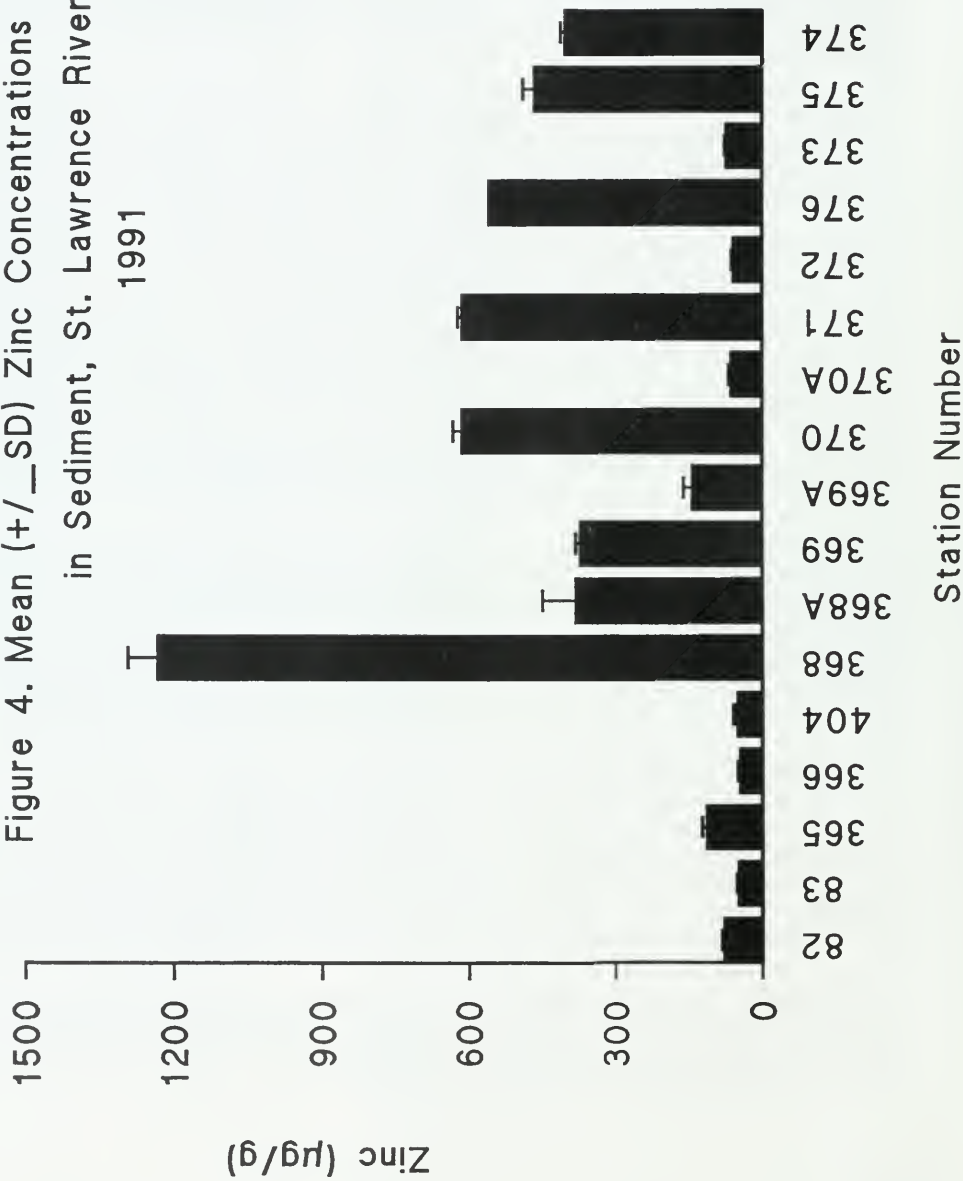


Figure 5. Mean (\pm SD) Lead Concentrations ($\mu\text{g/g}$)
in Sediment, St. Lawrence River,
1991

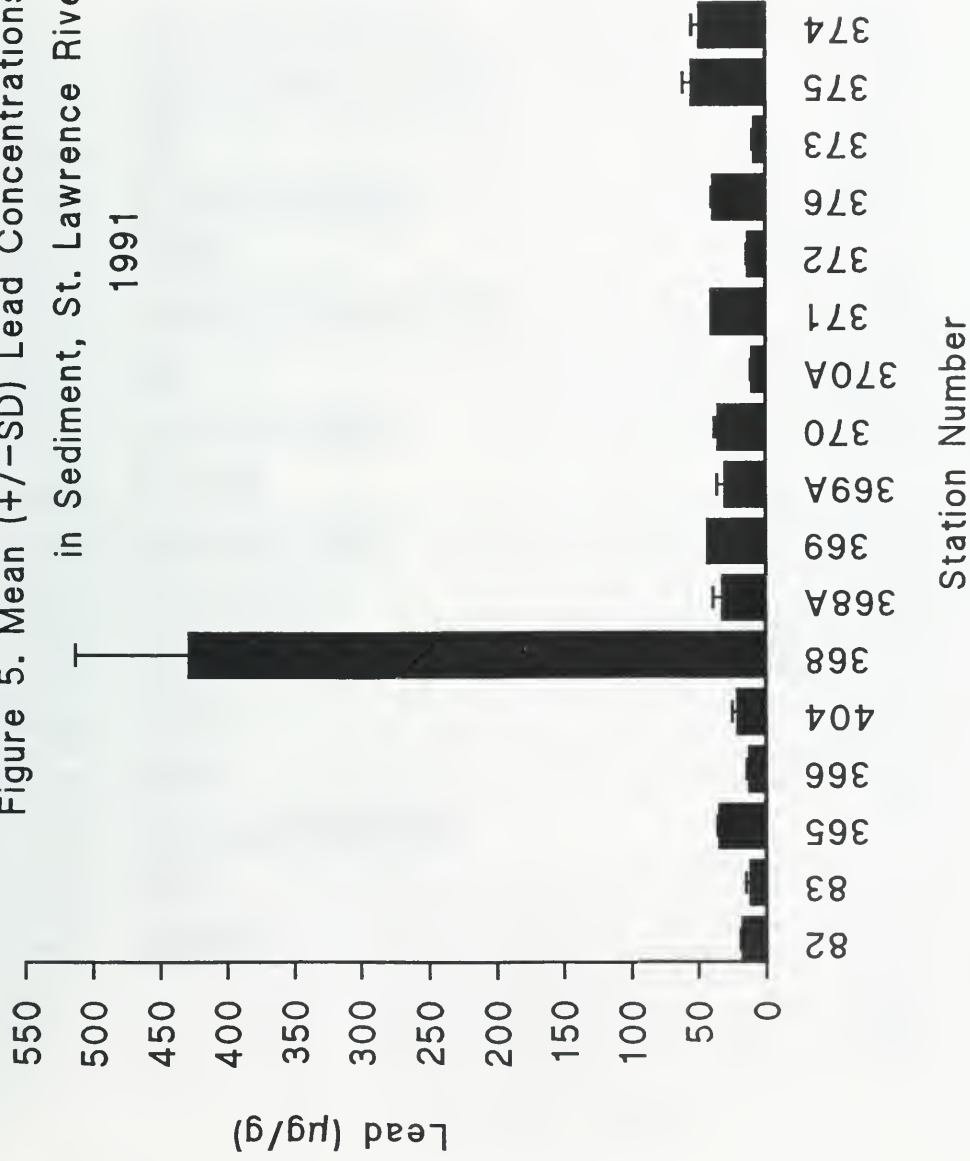
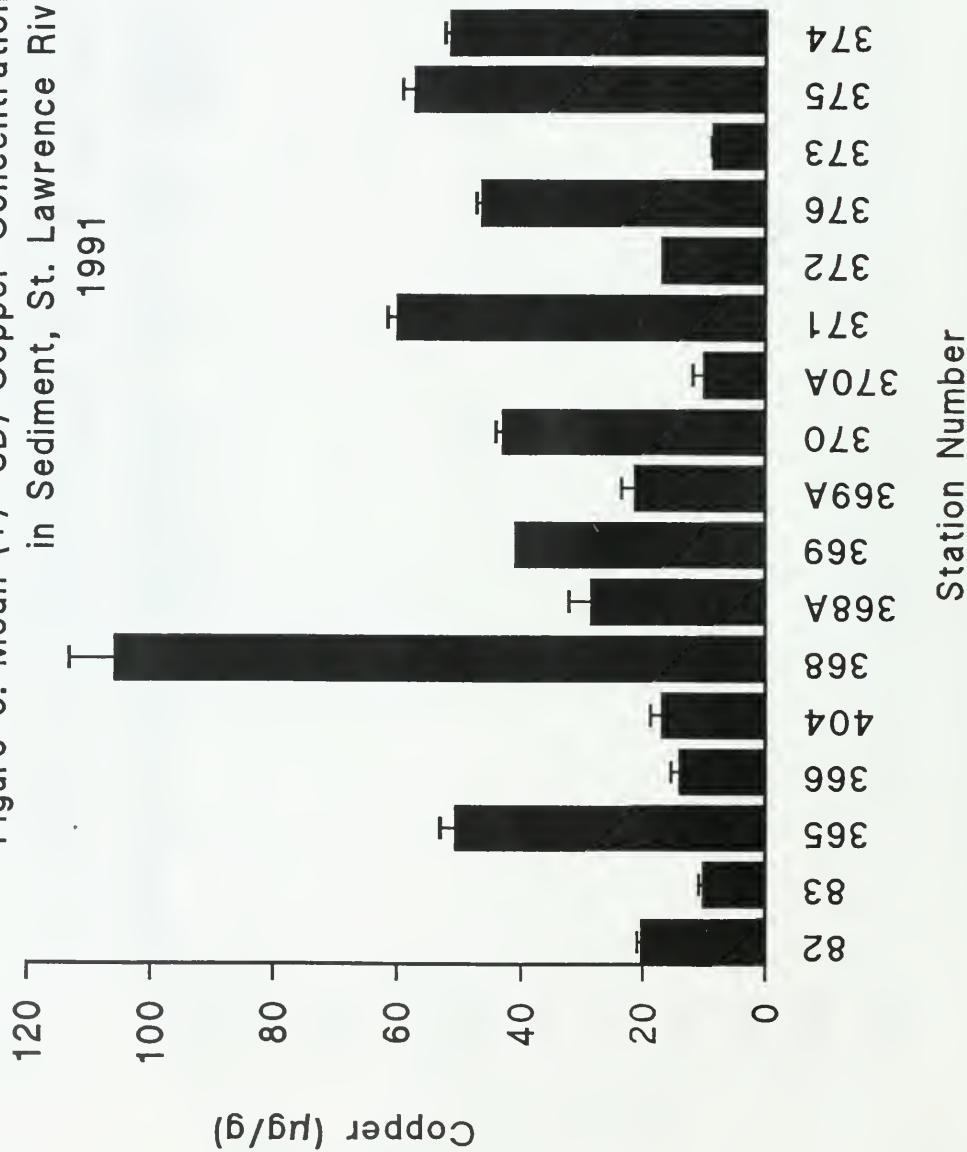


Figure 6. Mean (+/-SD) Copper Concentrations ($\mu\text{g/g}$)
in Sediment, St. Lawrence River,
1991



Particle Size Corrections

The heterogenous nature of the sediment in the St. Lawrence River makes it necessary to account for the different particle size distributions at individual sampling stations to compare contaminant concentrations between stations and identify trace metal contaminant sources. Based on particle size corrections there does not appear to be a significant local source of chromium, nickel, arsenic, iron, aluminum, manganese or cadmium in the area of concern. Following the regression analysis for sediment metal concentrations and percent particle size (clay plus silt), there were no significant differences between residuals from all stations for cadmium, chromium, nickel and copper (one way ANOVA). Differences in residuals between stations for arsenic, iron, aluminum and manganese were limited to only one or two stations and did not correspond to any sources. These results likely reflect the variability or range in contaminant concentrations for the area in general. Sediment metal concentrations at upstream reference stations were consistent with metal concentrations (and nutrients) found in sediment collected near Wolf Island (Persaud *et al.* 1989) at the head of the St. Lawrence River. Only cadmium concentrations in sediment were lower at Wolf Island than concentrations at the Lake St. Lawrence reference stations and downstream stations.

Particle size corrected data do not highlight Courtaulds' outfalls as a source of zinc, lead or copper despite the extremely high concentrations in the sediment and known effluent concentrations. Since this sampling site is so high in fine particles the statistical method of correction may have diminished the effect of the high concentrations of contaminants. The regression analysis was repeated after removal of station 368 from the data set to determine if the r^2 would improve. An improvement in the r^2 would indicate that metal concentrations at the site have skewed the data i.e the metal concentration was higher than expected based on percent fine particles. This was in fact the case for zinc, lead and copper. For example, based on the original regression equation for zinc the predicted zinc concentration in sediment at station 368 would be 549 $\mu\text{g/g}$ rather than 1233 $\mu\text{g/g}$ zinc actually present in sediment (Figure 7 and 8).

Another data correction method used, normalizes the anthropogenic trace metal results to a "conservative" element such as aluminum (i.e. an element that is not believed to be anthropogenic in origin). The ratio of the metal to aluminum should remain constant across a gradient of particle sizes unless there is an enrichment of the metal (Forstner 1990). For copper and lead the ratios were consistent at all stations except at station 368 where the ratio was ten times greater than at all other stations (Table A7). The ratio of zinc in sediment to aluminum sediment concentrations at stations upstream of station 368 were one hundred times lower than at station 368 and ten times lower than at all stations downstream of Courtaulds Fibres.

Figure 7.

Zinc Concentrations in Sediment (at all stations)
vs Percent Fine Particle size

$$r^2 = 0.4647$$

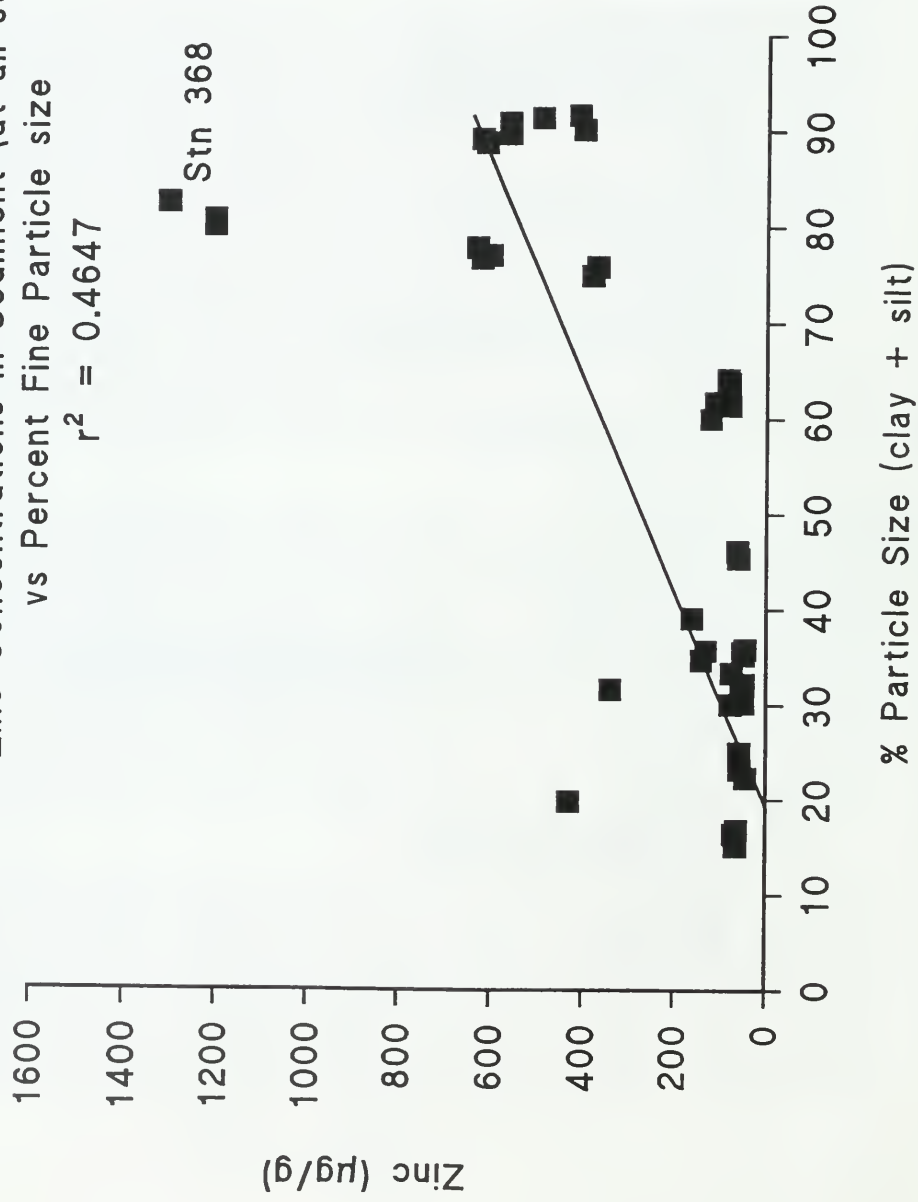
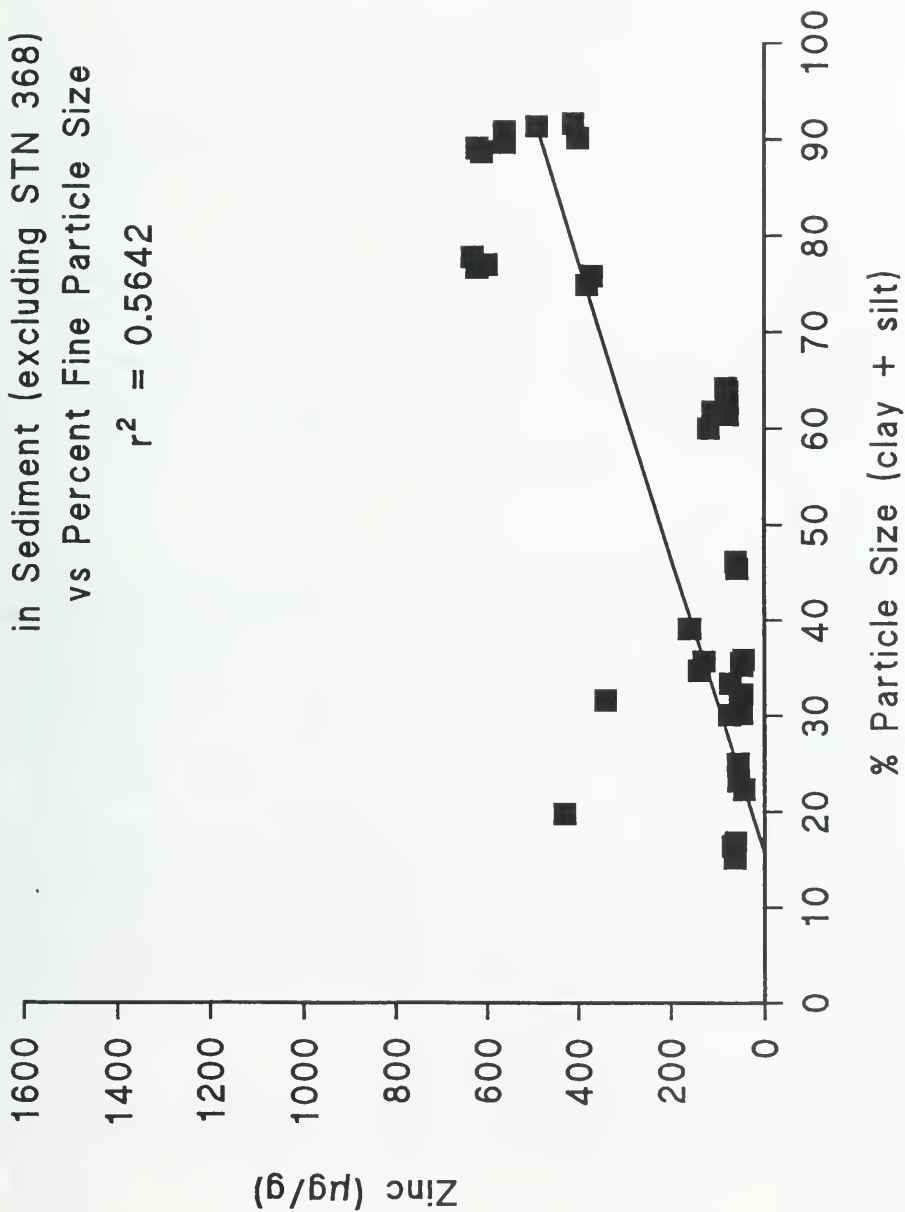


Figure 8. Zinc Concentrations
in Sediment (excluding STN 368)
vs Percent Fine Particle Size

$$r^2 = 0.5642$$



There was no relationship between particle size and mercury or methyl mercury concentrations in the sediment so particle size correction of the data was not appropriate. The high concentrations of mercury at several stations suggest several sources and general contamination throughout the area. Stations close to known point sources of mercury, however, do have a higher ratio of sediment mercury concentrations to aluminum concentrations than stations sampled farther downstream Table A7.

Nutrient Concentrations in Sediment.

The LEL was exceeded at all sites (including reference sites) for phosphorus and total kjeldahl nitrogen (TKN) and all but one site for total organic carbon (Table 4, A8). Twenty seven percent of the sediment samples exceeded the SEL for TKN. Sediment concentrations of TKN were significantly higher (Tukey's Studentized Range Test $p < 0.05$) at several stations when compared with the reference stations, however, when the data were corrected for particle size, concentrations of phosphorus and TKN in the sediment downstream were not significantly higher than the upstream reference sites. TOC content ranged from 1% to 7.5%.

Correlation Analysis.

For almost all variables tested, contaminant concentrations in sediment were highly correlated with one another ($p < 0.0001$) and with sediment nutrient concentrations, sulphur, loss on ignition and TOC. The correlation coefficients ranged from 0.79 to 0.95 for almost all variables. In some cases the r values were lower but still significant. The only exceptions were lead, mercury and methyl mercury which were not highly correlated with other metals or nutrients (r values were less than 0.7 and in many cases less than 0.6). In the case of mercury, correlations with many variables, (methyl mercury - all variables), were not statistically significant.

All variables with the exception of mercury and methyl mercury were also positively correlated with sediment particle size ($p < 0.0001$). Correlation coefficients were between 0.8 and 0.9 with only a few r values between 0.7 and 0.8. For lead, the correlation coefficients were low and ranged between 0.56 and 0.62. The lack of a correlation between mercury and particle size is an indication that mercury was enriched beyond the classical particle size/contaminant concentration relationship since fine suspended matter is known to have the greatest capacity to adsorb dissolved mercury (D'Itri 1990).

A principal components analysis (PCA) was performed using the mean value for each station for all the variables (Table 5). The first axis grouped all variables together with the exception of lead, mercury and methyl mercury. This axis explained 74.7% of the variation in the data. The first axis describes a gradient in sediment

Table 4: Mean [Standard Deviation] Concentration of Nutrients and Physical Parameters in Sediment Collected From the St. Lawrence River, 1991.

Station Number	N	Phosphorus (mg/g)		TKN (mg/g)		LOI (mg/g)		TOC (mg/g)		SULPHUR (%)	
		Mean	[S.D.]	Mean	[S.D.]	Mean	[S.D.]	Mean	[S.D.]	Mean	[S.D.]
82	3	0.96	0.04	2.55	0.18	51.17	2.93	27.17	1.89	0.11	0.02
83	3	0.85	0.03	1.10	0.10	19.33	0.58	10.60	1.22	0.05	0
365	2	0.87	0.02	4.45	0.21	115.00	7.07	75.50	0.71	0.49	0.03
366	3	0.77	0.08	1.85	0.09	32.0	1.0	16.17	2.56	0.12	0.004
404	3	0.69	0.05	1.30	0.10	25.33	1.53	15.33	0.58	0.16	0
368	3	0.97	0.03	3.01	0.32	66.30	3.78	35.33	3.05	0.68	0.08
368A	2	0.91	0.09	2.55	0.49	44.00	7.07	26.00	2.83	0.20	0.01
369	2	1.20	0.14	4.15	0.07	76.00	1.41	38.00	1.41	0.38	0.04
369A	3	0.89	0.07	2.08	0.08	38.80	9.25	23.55	4.44	0.22	0.03
370	3	1.20	0.10	7.60 ▲	0.52	103.00	6.08	52.33	0.58	0.47	0.02
370A	3	0.59	0.04	0.98	0.12	24.33	1.15	14.00	1.00	0.10	0.01
371	2	1.20	0	6.20 ▲	0	96.50	0.71	55.50	7.78	0.48	0.01
372	2	0.88	0.10	2.75	0.07	38.00	0	19.00	0	0.18	0.02
376	2	1.25	0.07	7.25 ▲	0.49	110.00	0	60.00	1.41	0.54	0.02
373	2	1.00	0.01	1.35	0.07	23.50	0.71	12.50	0.71	0.05	0
375	3	1.33	0.11	5.87 ▲	0.29	94.33	3.21	49.67	1.52	0.43	0.04
374	2	1.15	0.07	6.65 ▲	0.35	115.00	7.07	56.50	2.12	0.57	0.03
Lowest Effect Level		0.600		0.550				1 %			
Severe Effect Level ▲		2.00		4.80				10 %			

Table 4 Continued

Station	N	SUM 1: % Clay (0.17 - 2.63 μm)		SUM 2: % Silt (2.63 - 62 μm)		SUM 3: % Sand (62 - 999 μm)	
		Mean	[S.D.]	Mean	[S.D.]	Mean	[S.D.]
82	3	5.06	0.68	58.03	1.40	35.16	1.34
83	3	2.06	0.15	29.13	1.10	68.37	1.15
365	2	5.10	0.72	55.75	0.49	34.55	0.78
366	3	4.10	0.41	31.43	0.11	59.37	0.72
404	3	2.01	0.09	21.50	1.44	70.57	0.86
368	3	8.38	2.72	72.60	2.56	18.12	1.16
368A	2	2.85	1.24	22.85	7.14	61.00	18.10
369	2	8.60	0.01	66.75	0.64	20.50	0.42
369A	3	3.80	0.25	32.70	2.18	61.90	2.36
370	3	11.10	1.30	66.07	1.76	18.17	0.65
370A	3	1.88	0.04	14.23	0.83	77.50	3.47
371	2	13.25	0.49	75.65	0.21	9.64	0.25
372	2	5.57	0.38	40.20	0.14	53.10	0.42
376	2	10.03	2.36	80.20	1.56	8.36	0.91
373	2	3.88	0.70	27.85	1.63	66.80	2.12
375	2	13.1	0.14	79.85	0.07	6.35	0.04
374	2	13.05	0.49	77.80	1.56	8.18	0.92

Table 5. Component Loadings and Percent of Total Variance Explained for the PCA of Sediment Quality.

Parameter	PC I	PC II	PC III
Aluminum	0.950	-0.232	0.032
Arsenic	0.969	-0.154	-0.101
Cadmium	0.963	-0.026	-0.090
Chromium	0.961	0.162	0.161
Copper	0.831	0.504	0.193
Iron	0.950	-0.168	-0.002
Manganese	0.851	-0.229	-0.122
Nickel	0.980	-0.069	-0.054
Lead	0.379	0.748	0.532
Selenium	0.955	0.110	0.070
Zinc	0.752	0.473	0.355
TKN	0.913	-0.276	-0.163
Total Phosphorus	0.851	-0.326	0.100
LOI	0.926	-0.090	-0.289
Sulphur	0.924	0.301	-0.015
TOC	0.866	-0.012	-0.403
Mercury	0.379	0.749	-0.376
Methyl Mercury	0.099	0.676	-0.659
Clay	0.934	-0.226	0.091
Silt	0.957	-0.098	0.117
Sand	-0.980	0.092	-0.059
Clay + Silt	0.963	-0.115	0.113
	74.7%	11.9%	6.4%
Percent Total Variance Explained			

quality among stations and was also influenced by sediment physical features such as percent sand, silt and clay. Nutrients, physical parameters and all the metals with the exception of lead, mercury and methyl mercury were highly correlated with the first axis.

Lead, mercury, methyl mercury and to some extent copper were highly correlated with the second axis while the third component summarized patterns in methyl mercury and lead. Methyl mercury scored negatively and lead scored positively on this axis. By including these three axis, 86.6% and 93.5% of the variability was explained respectively.

The station distribution pattern consisted of four groups (Figure 9). In general station 368 was isolated because of high concentrations of copper, lead and mercury on all three axes. Station 370, 371, 374, 375, 376, 365 and 369 were grouped together on PC I since these stations tend to be higher in most metals and percent fine sediment than the reference stations and station 366, 368A, 369A, 370A, 372, 373 and 404 which were correlated negatively on PC I. Station 368A, 369A, 370A and 404 scored positively on PC II since concentrations of mercury and methyl mercury tended to be greater than concentrations present at the other stations within that group.

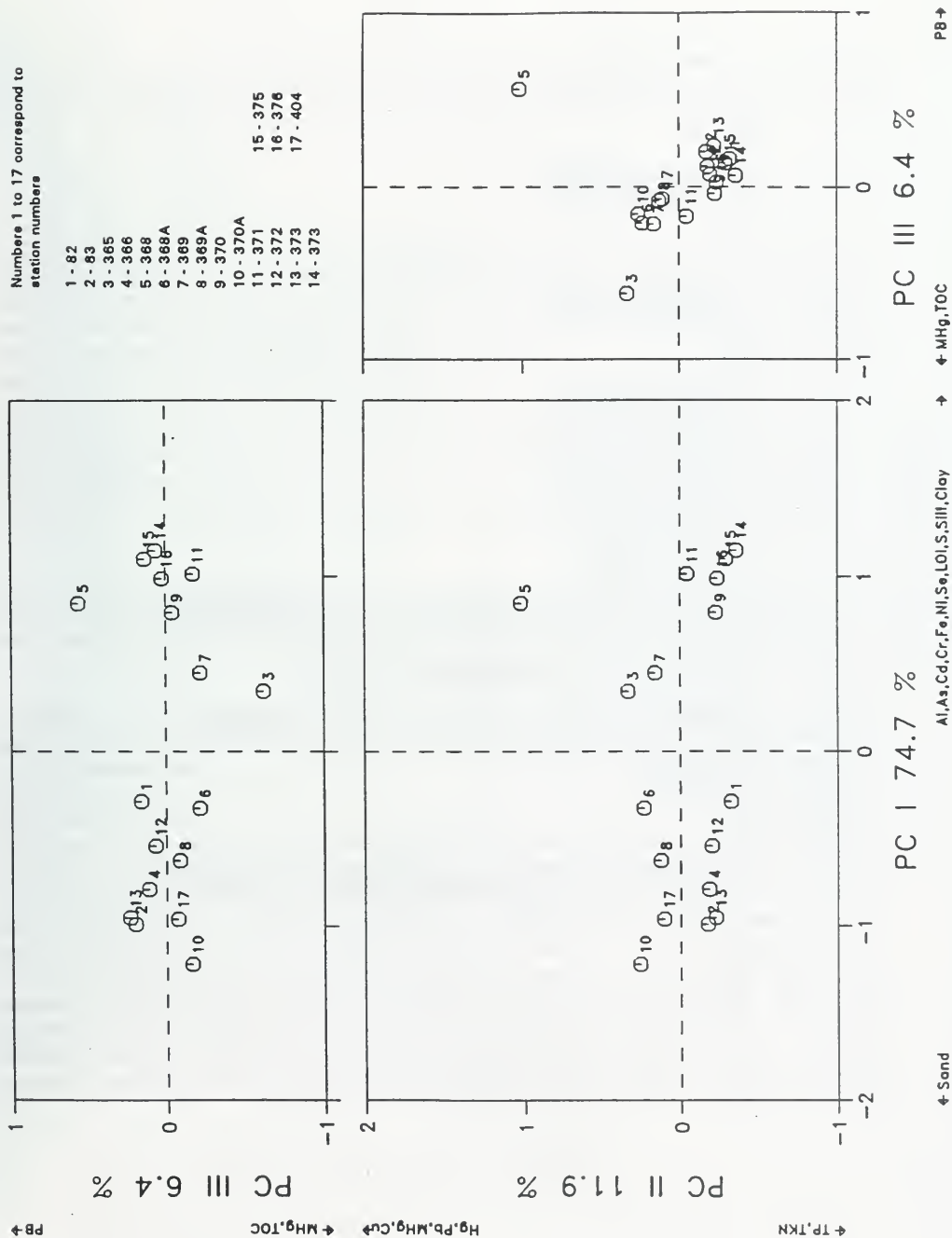
Station 365 and 369 were separated from the stations with the higher metal concentrations on PC II likely because of the higher mercury and copper concentrations present in the sediment at those two sites.

On PC III, station 365 falls out of the cluster of stations likely because of the high methyl mercury concentrations. The remaining stations fall into two groups based on sediment methyl mercury concentrations.

Comparison of 1991 Sediment Results With Historical Data.

A qualitative comparison between data from 1991 and 1985 shows that contaminant concentrations have increased at some stations and decreased at others without a consistent pattern. The only exceptions are stations 369, 371 and 374 where increases in contaminant concentrations in 1991 were seen for all contaminants analyzed. The changes in contaminant concentrations observed were likely due to sample differences in percent fine particles rather than changes in local or upstream contaminant loadings. The percentage of clay plus silt in 1985 at station 369 was 18% compared with a mean of 74% [standard error; SE 0.37] in 1991 and the percentage of fine particles at station 371 and 374 were 26% and 14% respectively in 1985 as compared with mean values of 89% [SE 0.16] and 91% [SE 0.61] in 1991.

Figure 9. PCA of Sediment Quality Data for all Stations Illustrating PCI, PCI and PCIII.



Overall, the percentage of stations with contaminant concentrations above the LEL for biotic impact is similar between 1991 and 1985. The only exception is lead and cadmium with more stations exceeding the guideline in 1991 than in 1985.

Mercury in Sediment

Total mercury and methyl mercury were measured in sediment at each station. The one way ANOVA found a significant difference ($p < 0.0001$) in mean mercury and methyl mercury concentrations in sediment between stations. Concentrations of total mercury were higher in sediment collected adjacent to, and downstream of known mercury sources when compared with upstream stations. Concentrations of total mercury in sediment decreased with increasing distance from sources at a steeper rate than methyl mercury but remained above background concentrations farther downstream of sources than sediment methyl mercury concentrations (Figure 10). In contrast, methyl mercury concentrations in sediment were elevated below the Domtar/ICI/Cornwall Chemicals LTD. diffuser and remained consistently high downstream of this source and Courtaulds Fibres for a longer distance than inorganic mercury (Figure 11) but then returned to background concentrations.

Tukey's Studentized Range Test showed that total mercury in sediment at stations 365, 368, 368A, and 369 were not significantly different, however, mean mercury concentrations at these four stations were significantly ($p < 0.05$) higher than concentrations present at all the other stations.

Station 365 is about 1.2 km downstream of the Domtar/ICI/Cornwall Chemicals diffuser. It was historically contaminated with mercury, although concentrations have decreased since the 1970's (Kauss *et al.* 1988). The mean mercury concentration in 1991 was 3.26 [SD 0.46] $\mu\text{g/g}$ which is thirty times greater than sediment mercury concentrations at the upstream reference stations (Table 3). In 1970, 1975 and 1979 mean mercury concentrations were 4.7, 5.69 and 6.8 $\mu\text{g/g}$ respectively, however, the range in mercury concentrations was from 0.05 to 19.8 $\mu\text{g/g}$ (Kauss *et al.* 1988). The concentration of mercury in sediment in 1985 was lower (0.630 $\mu\text{g/g}$) than in 1991, however, only a single sample was collected in 1985. Plume tracking models developed for the Domtar/ICI/Cornwall Chemicals diffuser show that the sampling area would be impacted by the effluent (Nettleton 1994). The mercury at this site now is likely due to effluent from the ICI chlor-alkali plant (OMOE 1992b). Mercury containing fungicides are no longer in use by Domtar, consequently, Domtar's effluent is low in mercury relative to the other point sources (OMOE 1993) and historical concentrations. Sediment cores might indicate if the more contaminated material from the 1970's is buried or has been transported downstream.

Figure 10. Mean (\pm SD) Mercury Concentrations ($\mu\text{g/g}$)
in Sediment, St. Lawrence River,
1991

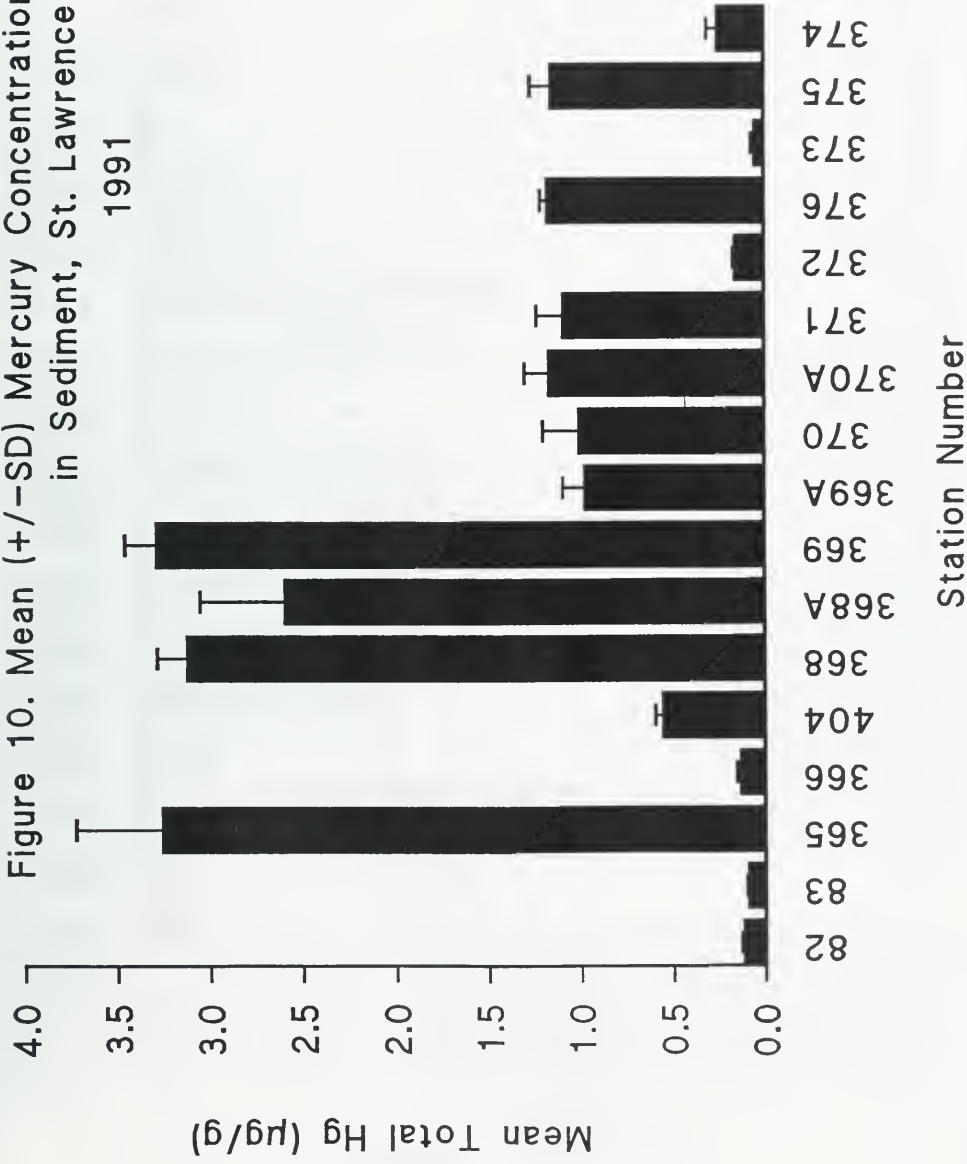
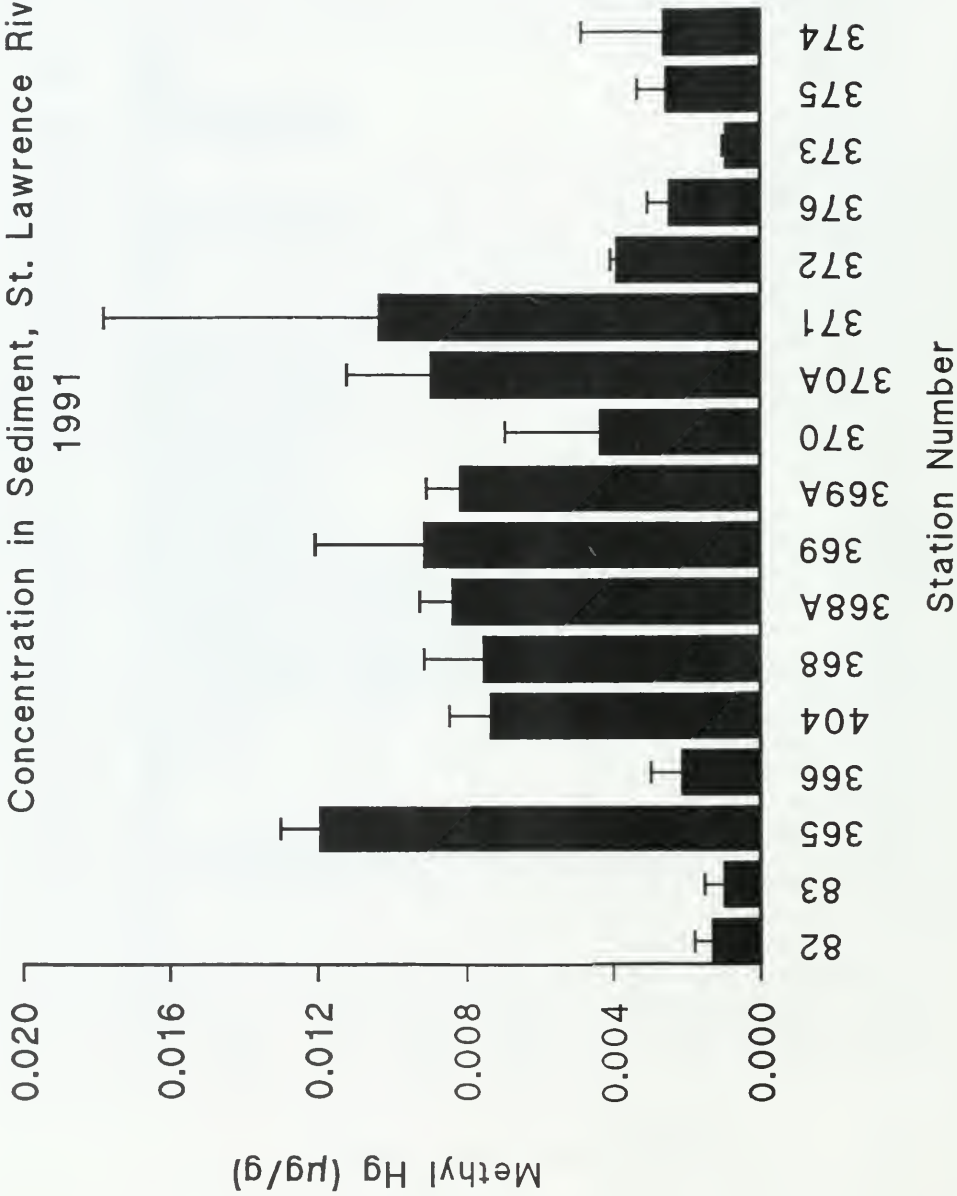


Figure 11. Mean (\pm SD) Methyl Mercury ($\mu\text{g/g}$)
Concentration in Sediment, St. Lawrence River,
1991



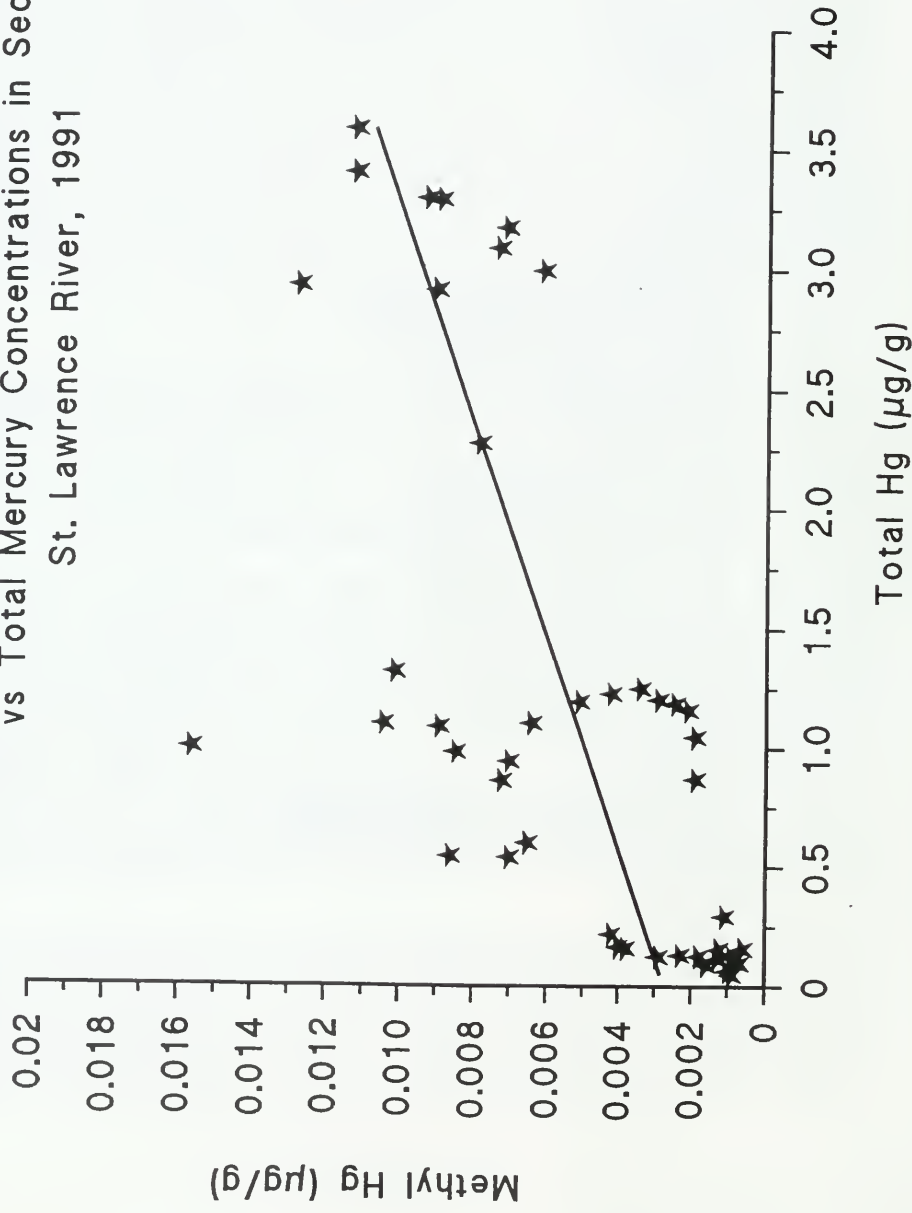
Station 368 is immediately downstream of Courtaulds fibre's shore based outfalls and stations 368A and 369 are about 50 m and 550 m downstream of the Courtaulds' diffuser respectively. Based on MISA data (OMOE 1992a), Courtaulds discharged the highest loading per year of mercury in the area of concern. This is believed to be due to mercury contamination of the sulphuric acid used in the rayon manufacturing process. Historically the caustic soda and wood pulp used by Courtaulds were also contaminated with mercury (J. Harwood personnel communication). These stations have also historically been high in sediment mercury concentrations and similar to station 365, are now lower than in 1975 and 1979. This decrease likely reflects the use of the diffuser which distributes the mercury downstream rather than discharging all the mercury at the nearshore. Concentrations of mercury in sediment at the shoreline in 1991 (mean 3.13 [SD 0.15] $\mu\text{g/g}$) are consistent with 1985 data (4.4 $\mu\text{g/g}$).

All stations downstream of the mercury sources have significantly higher ($p < 0.05$ - Tukey's Studentized Range Test) mercury concentrations than upstream reference stations with the exception of station 373 and station 374 and 366 which are open water stations where the current may be too fast for extensive sediment deposition and mercury accumulation. Station 372 has the same sediment mercury concentration as the reference stations. This station is influenced by sources on the south channel rather than the north channel (McCorquodale *et al.* 1992).

There was a significant difference in the sediment methyl mercury concentration between stations ($p < 0.0001$ - one way ANOVA). All stations immediately downstream of the mercury sources had significantly higher concentrations of methyl mercury in sediment than concentrations found in the upstream reference sites. Station 365 (downstream of the ICI mercury source) had the highest concentration of methyl mercury when compared to many stations, although concentrations were not significantly different than a second group of stations immediately downstream of station 365 (from station 404 to station 371) (Figure 11). Stations within this second group had significantly higher ($p < 0.05$) sediment methyl mercury concentrations than a third group of stations; the upstream reference sites and station 366 and 373 (similar to results for sediment total mercury concentrations) (Tukey's Studentized Range Test).

Methyl mercury concentrations in sediment were significantly ($p < 0.0001$) correlated with total mercury in sediment (r value 0.68204) suggesting biomethylation of available inorganic mercury (Figure 12). Bartlett and Craig (1981) found a similar relationship as well as Jackson (1986) in the Moose Jaw River Qu'appelle River System, however, Jackson found stronger correlations between methyl mercury and nutrients. Other studies have found poor correlations between sediment mercury

Figure 12. Methyl Mercury Concentrations in Sediment
vs Total Mercury Concentrations in Sediment
St. Lawrence River, 1991



and methyl mercury concentrations (Jackson *et al.* 1982, Mikac *et al.* 1985). Methyl mercury was not correlated with any other variables in the St. Lawrence River. Although total mercury was significantly correlated with TOC ($r=0.56$) and LOI ($r=0.52$). Percent methyl mercury was consistent with percentages found in other studies (Olson and Cooper 1975; Bartlett and Craig 1981; Mikac *et al.* 1985; Langston 1982).

To determine if sediment chemical and physical parameters were behaving the same way at each station in terms of influencing the sediment mercury concentration, the correlation coefficients for the total-sample analysis and the between-class sample analysis were examined. The correlation coefficients from both analyses were similar or the same for the correlation between all sediment parameters with mercury and methyl mercury in sediment. This suggests that the variability at individual stations is low. The results show that the relationship between mercury and methyl mercury in sediment with all the other metals and nutrients is the same at each station (i.e. for the variables tested, there are no parameters that are influencing mercury or methyl mercury concentrations in sediment differently at any one station).

Studies in the Wabigoon/English river system suggest that partitioning of inorganic mercury and methyl mercury between surface sediment, water and suspended particles occurs within days (Rudd and Turner 1983; Parks and Hamilton 1987; Parks *et al.* 1989). Inorganic mercury entering the water from the Cornwall point sources will be scavenged by particulate matter (in the effluent and in the water column), with the larger particulates deposited in the sediment relatively close to the source and the finer mercury contaminated particles deposited farther downstream.

The free mercury released from the sediment pool (and mercury in the water column either bound or soluble), will be transformed by microorganisms to mono or dimethyl mercury (Wood, 1968; Jenson and Jernelov, 1969; Compeau and Bartha 1985, 1986). Methyl mercury diffuses into the water column where it is taken up by biota and partitions between particulate and soluble phases which can also move downstream. The methyl mercury released from the contaminated sediment close to the sources in the St. Lawrence River may preferentially bind to the fine grained particles present (particularly at station 368) and accordingly settle out farther downstream and become more evenly distributed with distance than inorganic mercury. Furthermore, inorganic mercury that has settled out downstream will also serve as a source for methyl mercury production. This may account for the distribution pattern of methyl mercury in sediment at the sites sampled.

The results in the St. Lawrence River are consistent with seasonal patterns observed in the Wabigoon River for suspended particulates and dissolved mercury (Jackson *et al.* 1982). A similar deposition pattern of inorganic mercury and methyl mercury was also observed by Jackson (1986) in the Moose Jaw River-Qu'appelle River system for suspended particulate material and composition of bottom sediment.

The absence of a relationship between sediment methyl mercury concentrations and sediment nutrients or organic carbon in the St. Lawrence River may be because samples were collected in the winter when productivity and microbial activity tend to be low. Differences in productivity between stations may not have been apparent because of reduced microbial activity and subsequently a correlation with methyl mercury concentrations in sediment was not observed. Several studies have reported that temperature affects both mercury and methyl mercury concentration in the water with the lowest concentration observed in the winter (Shin and Krenkel 1976; Wright and Hamilton 1982; Parks and Hamilton 1987; Parks *et al.* 1989).

Since the percent methyl mercury to total mercury tended to increase in the St. Lawrence River as total mercury in the sediment decreased, conditions for methyl mercury production by microorganisms may have been more favourable with increasing distance from the source. Concentrations of total mercury at stations 365, 368, 368A and 369 may have inhibited additional methyl mercury production by the microorganisms or more subtle differences between station nutrient concentrations, TOC or the presence of detritus may have affected methyl mercury production.

Mercury in Benthos.

Mercury concentrations in benthos are in Table 6. The ANOVA showed a significant difference ($p < 0.0001$) in the benthic mean mercury concentrations between stations (ANOVA). Tukey's test for significant differences showed that mercury in benthos at stations 368 and 368A were significantly higher than the mercury concentrations in biota at other stations. These two stations are extremely close to mercury sources, in particular station 368 which was placed immediately downstream of Courtaulds' shore based outfalls. Station 368A is about 50 m downstream of the Courtaulds' diffuser. Since benthos from the upstream reference station (station 82) had mercury concentrations similar to biota downstream of the sources, benthic tissue concentrations that appear to be high (station 365, 369 etc.) relative to other stations (for example station 83, 376, 373, 374 etc.) are likely within the natural range of variability among species from different stations (Figure 13).

The Pearson's Product Moment correlation revealed a significant positive relationship ($p < 0.0001$) between mercury concentrations in sediment and mercury in benthos ($r = 0.64304$) (Figure 14). A weak relationship was found between methyl mercury in sediment and mercury in benthos ($r = 0.53859$, $p < 0.0006$) (Figure 15), however, the bioavailability of the mercury appears to be related to proximity to the mercury source rather than the concentration of methyl mercury or total mercury in the sediment. The concentration of methyl mercury in sediment downstream of all the sources was not significantly different from the concentration in sediment collected from the Courtaulds site, although concentrations of mercury in benthos were significantly higher at Courtaulds than at the other stations. Other inconsistencies

Table 6. Mercury Concentrations (ng/g wet Weight) in Benthos Collected From the St. Lawrence River, 1991.

Station Number	Mercury in Benthos	Mean Mercury Concentration in Benthos [S.D.]
82	21.2	26.5 [4.9]
82	27.3	
82	30.9	
83	11.2	11.9 [2.0]
83	14.2	
83	10.4	
365	27.4	31.8 [4.4]
365	31.8	
365	36.3	
366	12.2	12.2 [0.5]
366	11.7	
366	12.7	
368	43.8	55.8 [26.8]
368	37	
368	86.5	
368A	96.4	68.0 [26.3]
368A	63.2	
368A	44.4	
369	21.4	24.3 [9.4]
369	16.7	
369	34.8	
369A	22.3	24.4 [7.8]
369A	33	
369A	17.8	
370	10.1	7.7 [2.3]
370	7.7	
370	5.4	
370A	24	24 [1.6]
370A	25.6	

Table 6 Continued		
Station Number	Mercury in Benthos	Mean Mercury Concentration in Benthos [S.D]
370A	22.3	
371	23.1	19.6 [3.0]
371	17.6	
371	18.2	
371 (split)	19.4	
372 (O)	5.5	6.4 [0.8]
372 (O)	7.1	
372 (O)	6.6	
372 (split) (O)	6.4	
376	14.4	14.0 [1.5]
376	12.4	
376	15.3	
376 (split)	15.2	
373 (O)	3.6	4.7 [0.9]
373 (O)	5.3	
373 (O)	5.1	
373 (split) (O)	5.8	
374 (O)	10.3	9.2 [1.0]
374 (O)	8.3	
374 (O)	9	
374 (split) (O)	8.15	

Benthos were not collected from Station 404 and 375.

(O) - Oligochaetes were collected at these stations. Chironomids were collected at all remaining stations.

Split - Samples are a duplicate sample and analysis (or mean of two duplicate analyses) of the previous sample listed.

Figure 13. Mean (\pm SD) Mercury Concentration
(ng/g wet weight) in Benthos,
St. Lawrence River, 1991

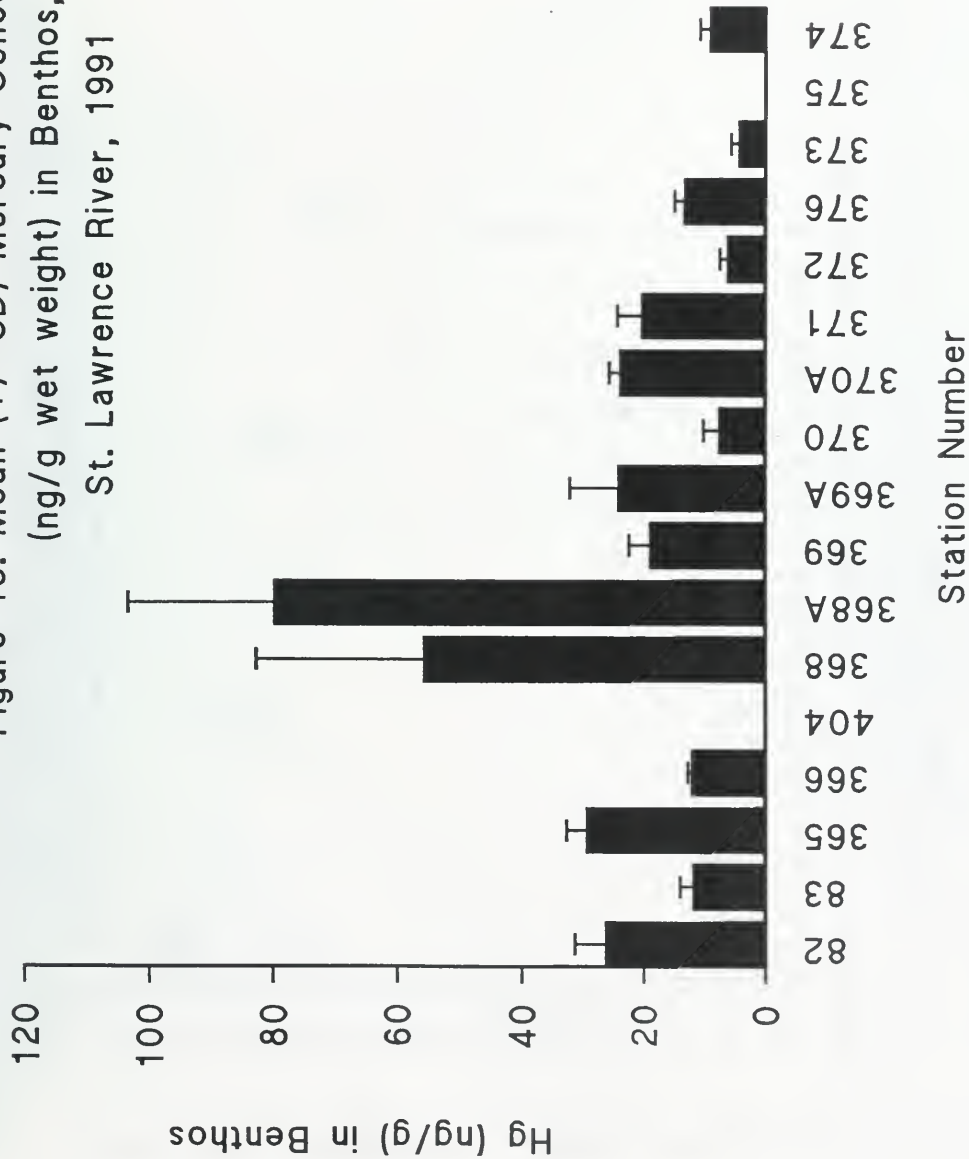


Figure 14. Mean Mercury concentration in Benthos
vs. Mean Mercury Concentration in Sediment
St. Lawrence River, 1991

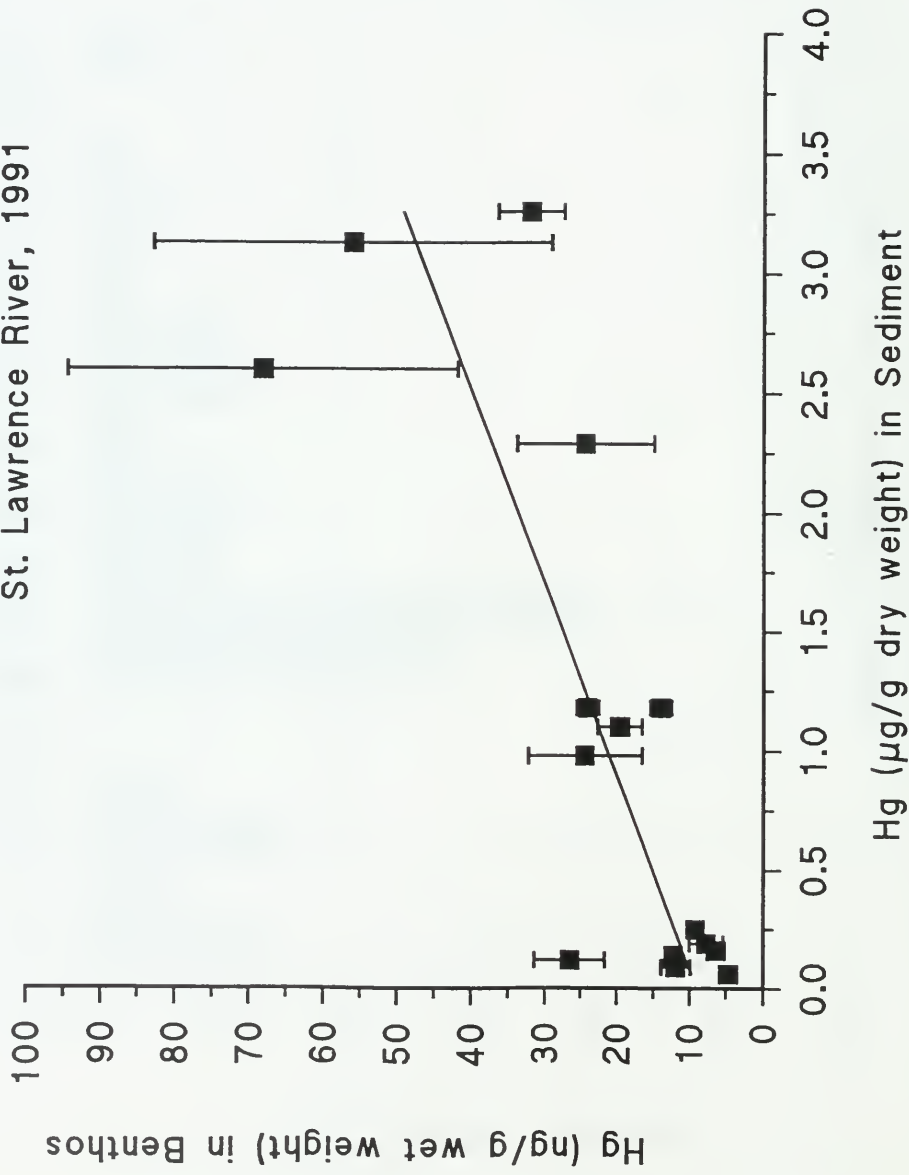
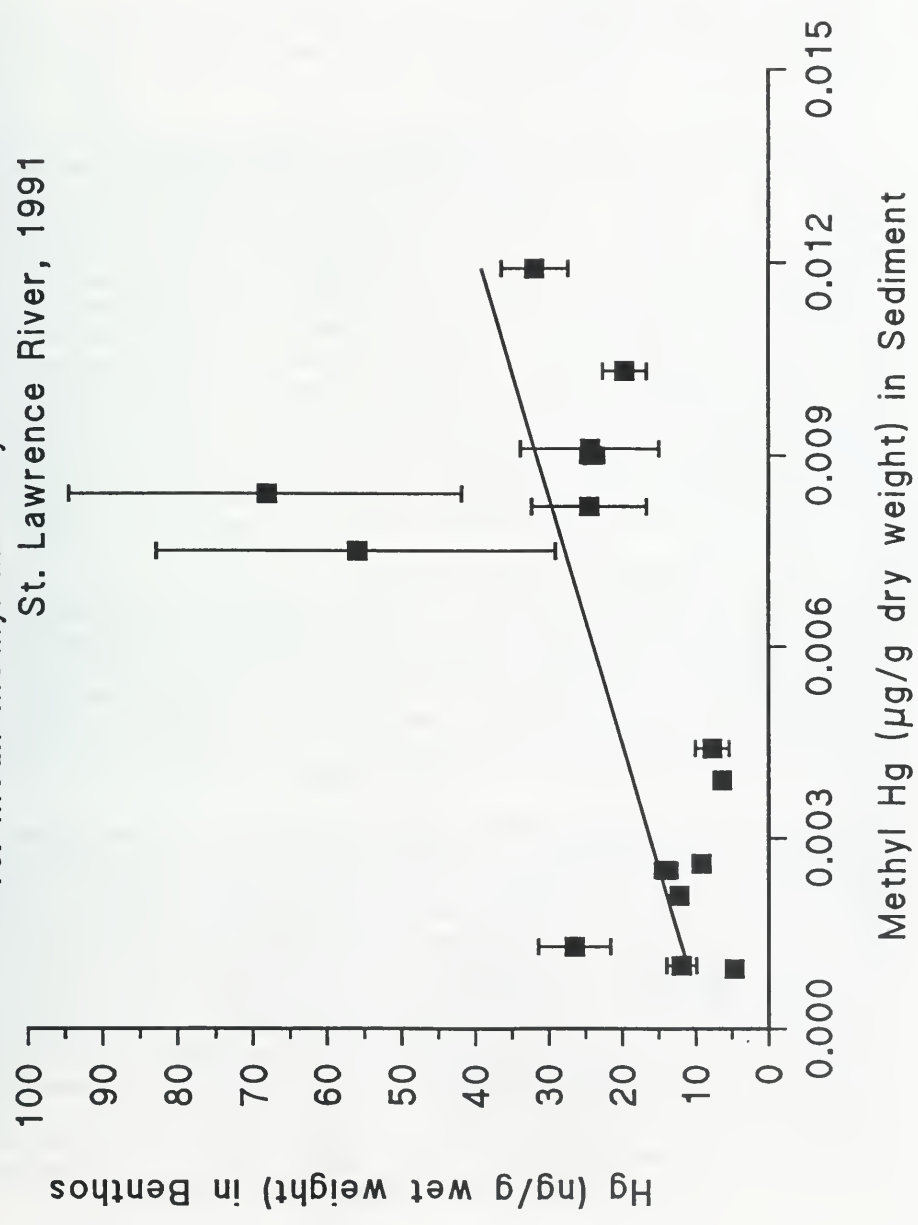


Figure 15. Mean Mercury Concentration in Benthos
vs. Mean Methyl Mercury Concentration in Sediment
St. Lawrence River, 1991



exist as well, for example, the total mercury concentration in the sediment at station 365 was significantly higher (Tukey's Studentized Range Test $p < 0.05$) than at the reference site; station 82, however, mercury concentrations in benthos were not significantly different between the two stations.

Mercury tissue concentrations in benthos have been correlated with sediment mercury in some studies (Hornung *et al.* 1984; Hornung 1989), however, there are several studies that have not found a relationship (Jernelov and Lann 1971; Rubinstein *et al.* 1983; Jackson 1988.). There are many factors which will influence mercury concentrations in biota. Accumulation of mercury is dependent on metabolic rate, feeding habits, mercury speciation and chemical processes and perhaps even on the interaction of mercury with other metals and contaminants in the environment. Direct proportionality between sediment contaminant concentration and tissue residues are assumed despite evidence which indicates other parameters such as competing metals and organic material (Luoma 1977; Bartlett and Craig 1981) and physical parameters may modify bioavailability (Rubinstein *et al.* 1983; Luoma 1989; Landrum and Robbins 1990). The mercury content of aquatic organisms varies greatly among species from the same location and within species from different locations (Huckabee *et al.* 1979). Simple correlations between metal concentrations in the sediment and concentrations in deposit/detritus feeding biota are often weakly significant (Luoma 1983).

The route of exposure may be particularly important. The chironomids and oligochaetes are exposed to dissolved inorganic mercury and methyl mercury in the water column and pore water and through ingestion of metal enriched particulate matter. Because of the proximity of the source, biota at station 368 may have been exposed to more dissolved mercury and methyl mercury rendering it more bioavailable and resulting in significantly higher mercury tissue concentrations than in biota collected from other stations. The mercury that is deposited downstream is bound to particulates and may be initially less bioavailable.

Factors which affect bioavailability include: characteristics of the contaminants, composition and characterization of the sediment and behavioral and physiological characteristics of the organism (Landrum and Robbins 1990). Sediment characteristics which will enhance the sorption of contaminants and accordingly reduce their bioavailability include; organic carbon content, particle size distribution, clay type and content, cation exchange capacity, presence of sulphides and pH (Gavis and Ferguson 1972; Reimers and Krenkel 1974; Luoma, 1989; Landrum and Robbins 1990). Organic carbon content may have influenced contaminant uptake by benthos in the St. Lawrence River. A significant positive correlation was found between the mean mercury concentration in benthos and the ratio of total mercury concentrations in sediment to total organic carbon ($r = 0.7966$ $p < 0.0003$) (Figure 16). An even stronger relationship ($r = 0.8330$ $p < 0.0001$) was observed (Figure 17) between the mean mercury concentration in benthos and the ratio of total mercury concentrations

Figure 16. Mean Mercury Concentration in Benthos
vs Total Mercury in Sediment/Total Organic Carbon
St. Lawrence River, 1991

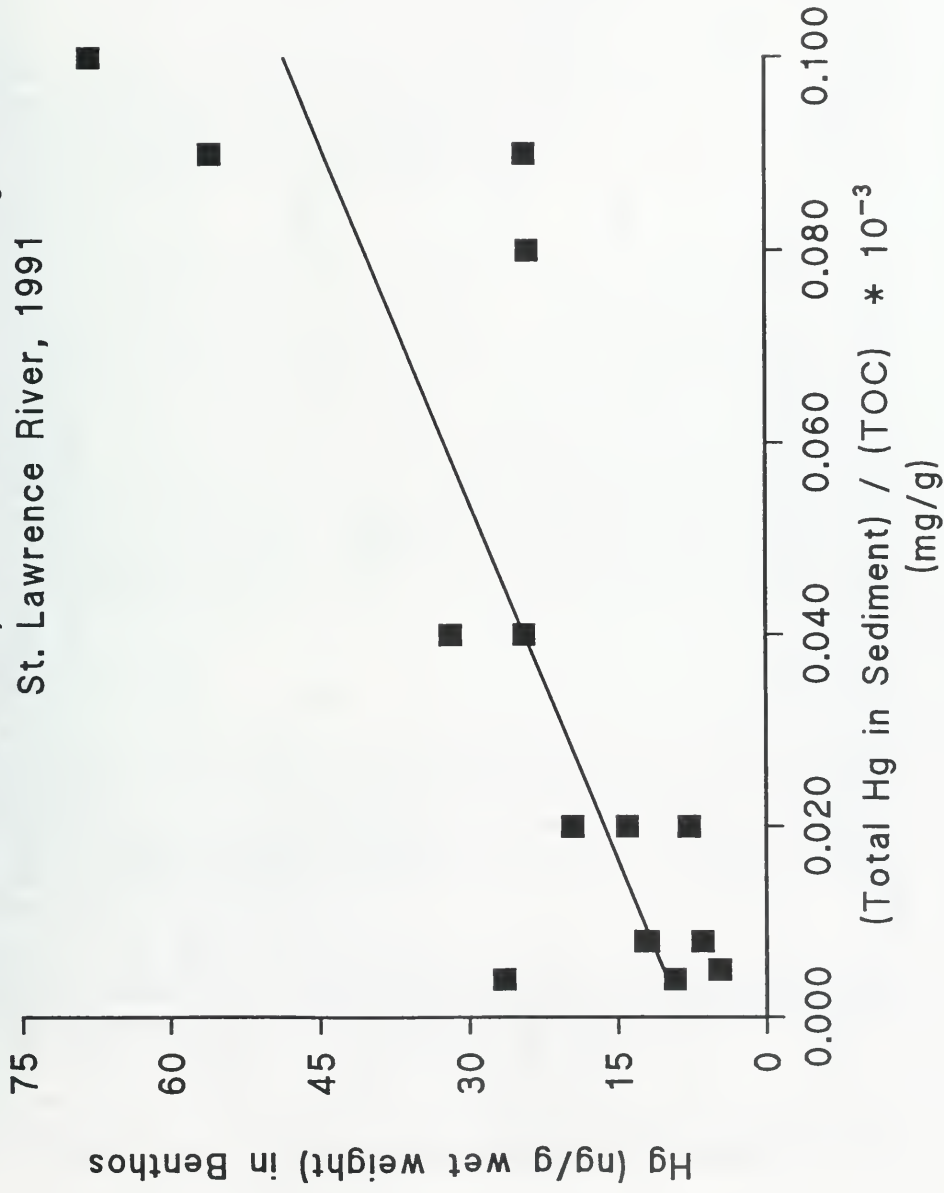
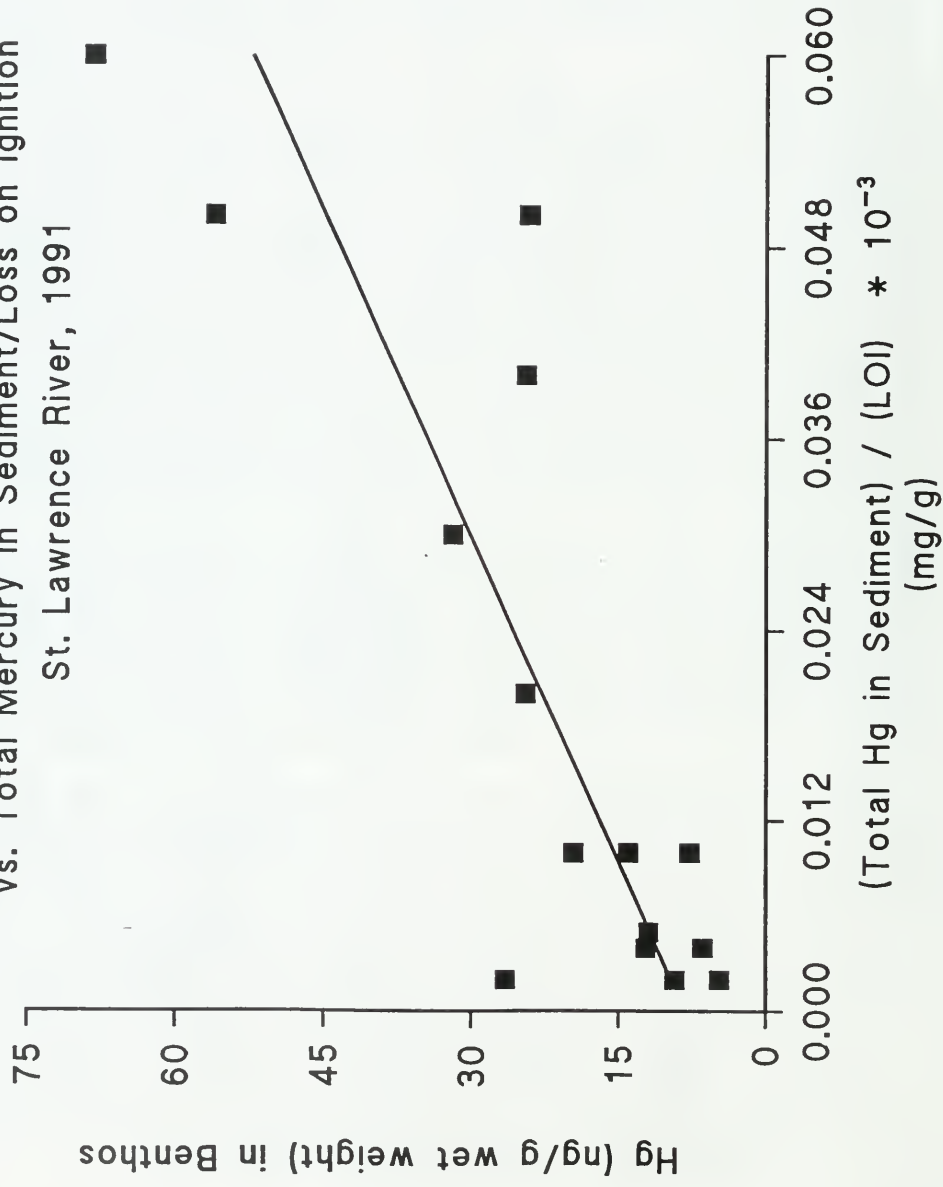


Figure 17. Mean Mercury Concentration in Benthos
vs. Total Mercury in Sediment/Loss on Ignition
St. Lawrence River, 1991



in sediment to loss on ignition (which is a reflection of the organic content of the sediment). Organic matter may have bound the mercury rendering it less bioavailable. The ratio of total mercury in sediment to TOC or LOI acts as a normalization of the sediment effectively removing the influence of the organic material and making comparisons between stations possible. This has been observed in several other studies investigating the bioavailability of mercury to invertebrates (Luoma 1977; Langston 1982; Jackson 1988). Total organic carbon in the sediment at station 365 was significantly higher than concentrations at the upstream reference stations and may have inhibited the mercury uptake in benthos at that station relative to the reference site.

Particle size may influence bioaccumulation since benthic organisms tend to feed on fine grain material which has a tendency to sorb the most contaminants. The potential exposure is expected to be greater than from bulk sediment concentrations. Particle size distribution and clay content (clay type was not investigated) did not appear to influence mercury bioavailability in the St. Lawrence River. There was no correlation between sediment total mercury or methyl mercury concentrations and particle size (silt, clay or sand), nor was there a correlation between mercury in biota and particle size. Benthos from station 368A had significantly higher mercury concentrations than benthos from other stations but had a relatively low percentage of fine particles (27% silt plus clay), although the concentration of total mercury was high. The pH was consistent at all sampling stations eliminating it as a variable which influenced bioavailability. Field data for cation exchange capacity (redox potential) were unreliable in general.

Sediment Bioassays

Sediment collected from station 82, 83, 368, 368A, 369, 370, 374 and 375 were used for sediment bioassays. A summary of the results from Bedard and Petro 1992 is as follows. The bioassays showed that, in general, sediment collected from stations downstream of the point sources of contaminants resulted in high organism survival but exerted sublethal growth effects to the benthic invertebrates *Hexagenia limbata* and *Chironomus tentans* when compared with sediment collected from the reference stations 82 and 83.

Sediment collected from station 368 and 368A (closest to Courtaulds outfall) caused a significant growth reduction and lower body weight in exposed mayflies and midges when compared with growth in biota exposed to sediment from reference sites and to biota exposed to sediment from all the other sites sampled.

Sediment from station 369 (downstream of station 368) also produced a significant reduction in growth and lower body weight for the midge exposures when compared with biota exposed to sediment from all the other stations. For midges, growth was

reduced by 33% at station 368A, 36% at station 369 and 89% at station 368 when compared with growth of midge larvae exposed to sediment from the reference stations. Exposure to sediment from station 368 also produced the highest percent mortality for mayflies and midges when compared with other stations, however, this was only significant in some cases. These results reflect the high concentration of metals in the sediment at these stations. The concentration of lead, zinc, copper and mercury were above the SEL in sediment collected from station 368 when analyzed for the bioassays which confirm the results previously described for the sediment survey. The sediment survey also found significantly higher concentrations of mercury at these three stations compared with all other stations sampled. The lethal and sublethal effects on organisms exposed to sediment from station 368, 368A and 369 are likely related to the high sediment metal concentrations.

Sediment from the reference stations 82 and 83 consistently supported the best growth in organisms and station 370, 374 and 375 consistently reported average growth. Sediment analysis for the bioassays for these stations were also consistent with results from the overall sediment survey.

Mayfly growth at station 368 and 368A was similar to the growth in mayflies exposed to sediment from Honey Harbour, Georgian Bay. This sediment is used as a "negative control" for each bioassay to provide a measure of test acceptability (i.e. if mortality in the negative control exceeds a designated level then the test is declared invalid). The similarity in results between mayflies at station 368 and 368A and the negative control may be due to prolonged storage of the negative control sediment or to a specific difference in the negative control sediment that is not representative of the study area.

Sediment from station 368 which caused poor growth in chironomid larvae and mayflies also caused the highest level of mortality in juvenile fathead minnows. Although the differences in percent mortality were not statistically significant, the data suggest that contaminants present in the sediment were also bioavailable to the fish. A comparison of contaminant tissue concentrations in minnows exposed to sediment collected from different stations confirm the bioavailability of the metals. The minnows exposed to sediment from station 368 had higher tissue concentrations of copper and lead than minnows exposed to all other sediment. Copper concentrations in minnows exposed to sediment from station 368 were, on average, 14.8 $\mu\text{g/g}$ compared to concentrations in minnows exposed to downstream sites with an average concentration of 7.4 $\mu\text{g/g}$. Lead concentrations in minnows from station 368 were eight times greater than concentrations in fish exposed to sediment from the other stations tested. Concentrations of mercury in tissue in minnows exposed to all stations downstream of the Lake St. Lawrence reference stations were higher than the tissue concentrations in minnows exposed to the control sediment, further illustrating the bioavailability of the mercury. Mercury concentrations in minnows at station 368 were higher than concentrations in minnows exposed to sediment from

the other stations. These results are consistent with results from the benthic survey where mercury in benthos at station 368 was significantly greater than mercury concentrations in benthos collected from other stations.

In summary, the bioassay results show that the sediment at station 368 is marginally toxic to *Chironomus tentans* larvae. The sediment from station 368 and 368A consistently elicited a sublethal response to both *Hexagenia limbata* and *Chironomus tentans* and station 369 caused sublethal responses to *Chironomus tentans*. In addition, tissue concentrations of lead, copper, zinc and mercury were higher in minnows exposed to sediment from station 368 than concentrations found in minnows exposed to other sediment. Sediment concentrations of these four metals were above the severe effect level at station 368. Sediment mercury concentrations were greater than the SEL at stations 368, 368A and 369. There is strong conclusive evidence that sediment contamination has a potential to impair native species particularly at station 368 and possibly at station 368A and 369. The results of the sediment bioassay are consistent with the field survey.

SUMMARY AND RECOMMENDATIONS

Sediment metal contamination is a concern in the St. Lawrence River, in general, due to a constant flow of contaminants from Lake Ontario. This is evident from the sediment contaminant results where "background" concentrations of several metals exceed the Ontario Provincial Sediment Quality Guidelines' "lowest effect level". However, the high mercury concentrations in sediment at stations downstream of the reference sites suggests an impact on environmental conditions in the St. Lawrence River from local point sources. The presence of higher concentrations of methyl mercury downstream of sources compared with upstream reference sites suggests the potential for continued contamination of the food chain. Furthermore, sediment concentrations of lead, zinc and copper exceeded the SEL at one station (368) downstream of Courtaulds Fibre shorebased discharges and concentrations of copper and zinc were elevated at several downstream stations.

The field data in conjunction with the data from sediment bioassays which show that sediment from station 368 and 368A consistently elicited a sublethal response to both *Hexagenia limbata* and *Chironomus tentans* and station 369 caused sublethal responses to *Chironomus tentans*, suggest that local contamination may have an impact on native biota. A comparison of contaminant tissue concentrations in minnows exposed to sediment collected from the different stations confirm the bioavailability of the metals present in the sediment.

Ongoing studies in the area of concern will investigate the stability and distribution of the sediment in the vicinity of station 368 to determine if the contaminated sediment is in a state of flux or if it remains in place. Furthermore, a detailed investigation is required to determine the volume of sediment that is contaminated so that appropriate remedial action can be planned.

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APPENDICES

Table A1: 1991 St. Lawrence River Sediment and Biological Assessment Station Latitude and Longitude.

Station Number	Latitude	Longitude	Distance From US Shore
0082	45°01'43"	74°51'30"	
0083	45°00'5"	74°53'43"	
0365	45°00'45"	74°43'46"	
0366	45°00'48"	74°43'08"	
0404	45°00'53"	74°42'43"	
0368	45°01'13"	74°41'38"	
0368A			580(m)
0369	45°01'18"	74°41'22"	
0369A			560(m)
0370	45°01'28"	74°41'00"	
0370A			840(m)
0371	45°01'40"	74°40'32"	
0376	45°01'38"	74°39'32"	
0373	45°02'6"	74°38'41"	
0375	45°01'54"	74°38'12"	
0372C	45°00'46"	74°39'44"	150(m)
0374	45°02'12"	74°37'00"	

Station # 362 45°00'37" 74°44'49"
 was used to collect sediment for gut clearing.

Table A2: Sediment Description

Station Number	Sediment Description
82	Silt and muck
83	Muck and detritus
365	Dark muck
366	Silt and dark muck
404	Dark muck mixed with tar and debris
368	Dark muck and detritus mixed with tar, fibres and silicone like debris
368A	As per station 368
369	Dark muck and detritus mixed with tar and fibres
369A	As per station 369
370	Dark muck, detritus and shells
370A	As per station 370
371	Dark muck and detritus
372	Dark muck, detritus and shells
376	Silt and dark muck
373	Clay and sand
375	Dark muck
374	Clay, sand and black muck
Five ponar grabs were taken for stations requiring chemical analysis. For stations requiring both chemical analysis and bioassessment 20 grabs were collected.	

Table A3: Concentration of Metals in Water Collected From the St. Lawrence River, 1991.
All samples were collected from 1m below the surface. There are three replicates per station.

Station Number	ALUMINUM mg/L	ARSENIC mg/L	CADMIUM mg/L	CHROMIUM mg/L	COPPER mg/L	IRON mg/L	MERCURY µg/L	MANGANESE mg/L	NICKEL mg/L	LEAD mg/L	ZINC mg/L
82	-	-	-	0.0010	0.0010	-	-	0.0020	-	-	0.0010
82	-	-	-	0.0010	0.0010	-	-	0.0020	-	-	0.0010
82	-	-	-	0.0010	-	-	-	0.0020	0.003	-	0.0010
83	-	-	-	0.0010	-	-	-	0.0030	-	-	0.0020
83	-	-	-	0.0010	0.0010	-	-	0.0030	0.003	-	0.0040
83	0.020	-	-	0.0010	0.0010	-	-	0.0030	0.003	-	0.0040
365	0.030	-	-	0.0010	0.0010	0.03	-	0.0040	0.003	-	-
365	0.030	-	-	0.0010	-	-	-	0.0030	-	-	-
365	0.080	-	-	0.0010	0.0010	0.100	-	0.0110	0.003	-	0.0010
366	-	-	-	0.0010	0.0010	-	-	0.0030	0.003	-	0.0020
366	-	-	-	0.0010	0.0010	-	-	0.0030	0.003	-	0.0020
366	-	-	-	0.0010	0.0010	-	-	0.0030	0.003	-	0.0020
Water Quality Objectives		0.1	0.0002	0.1	0.005	0.3	0.2 (filtered)		0.025	0.025	0.03
Method Detection Limit	0.01	0.001	0.0002	0.0005	0.0005	0.02	0.02	0.0005	0.002	0.005	0.0005

Table A3 continued

Station Number	ALUMINUM mg/L	ARSENIC mg/L	CADMIUM mg/L	CHROMIUM mg/L	COPPER mg/L	IRON mg/L	MERCURY μg/L	MANGANESE mg/L	NICKEL mg/L	LEAD mg/L	ZINC mg/L
404	0.030	-	-	0.0010	0.0010	-	-	0.0030	0.003	-	0.0010
404	-	-	-	0.0010	0.0010	-	-	0.0030	0.003	-	0.0010
404	-	-	-	0.0010	-	-	-	0.0030	-	-	0.0010
368	0.020	-	-	0.0010	-	-	-	0.0030	0.003	-	0.0120
368	0.020	-	-	0.0010	-	-	-	0.0030	0.003	-	0.0120
368	0.020	-	-	0.0010	-	0.040	-	0.0030	0.005	-	0.0110
368A	0.020	-	-	0.0010	-	-	-	0.0030	-	-	0.0090
368A	0.020	-	-	0.0010	0.0010	-	-	0.0030	0.003	-	0.0100
368A	0.020	-	-	0.0010	-	-	-	0.0030	0.003	-	0.0090
369	0.020	-	-	0.0010	0.0010	-	-	0.0030	0.003	-	0.0090
369	-	-	-	0.0010	0.0010	-	-	0.0030	0.003	-	0.0090
369	-	-	-	0.0010	0.0010	-	-	0.0030	-	-	0.0090
369A	-	-	-	0.0010	0.0010	-	-	0.0030	-	-	0.0030
369A	-	-	-	-	-	-	-	0.0030	-	-	0.0010
369A	-	-	-	0.0010	0.0010	-	-	0.0030	0.003	-	0.0020
Water Quality Objectives		0.1	0.0002	0.1	0.005	0.3	0.2 (filtered)		0.025	0.025	0.03
Method Detection Limit	0.01	0.001	0.0002	0.0005	0.0005	0.02	0.02	0.0005	0.002	0.005	0.0005

Table A3 continued

Station Number	ALUMINIUM mg/L	ARSENIC mg/L	CADMIUM mg/L	CHROMIUM mg/L	COPPER mg/L	IRON mg/L	MERCURY µg/L	MANGANESE mg/L	NICKEL mg/L	LEAD mg/L	ZINC mg/L
370	-	-	-	0.0010	-	-	-	0.0030	-	-	0.0050
370	-	-	-	0.0010	-	-	-	0.0030	-	-	0.0050
370	-	-	-	0.0010	-	-	-	0.0030	0.003	-	0.0050
370A	-	-	-	0.0010	0.0010	-	-	0.0030	0.003	-	-
370A	-	-	-	-	-	-	-	0.0020	-	-	-
370A	-	-	-	0.0010	0.0010	-	-	0.0030	0.003	-	-
371	0.020	-	-	0.0010	0.0010	0.030	-	0.0030	0.003	-	0.0090
371	-	-	-	-	0.0010	-	-	0.0030	0.003	-	0.0080
371	-	-	-	0.0010	0.0010	-	-	0.0030	0.003	-	0.0080
372	0.020	-	-	0.0010	-	0.030	-	0.0030	0.003	-	0.0010
372	-	-	-	0.0010	0.0010	-	-	0.0030	0.003	-	0.0010
372	0.020	-	-	0.0010	-	-	-	0.0030	-	-	-
376	0.020	-	-	0.0010	-	-	-	0.0030	0.003	-	0.0070
376	0.020	-	-	0.0010	-	-	-	0.0030	0.003	-	0.0070
376	0.020	-	-	0.0010	-	-	-	0.0030	0.003	-	0.0080
Water Quality Objectives		0.1	0.0002	0.1	0.005	0.3	0.2 (filtered)		0.025	0.025	0.03
Method Detection Limit	0.01	0.001	0.0002	0.0005	0.0005	0.02	0.02	0.0005	0.002	0.005	0.0005

Table A3 continued

Station Number	ALUMINUM mg/L	ARSENIC mg/L	CADMIUM mg/L	CHROMIUM mg/L	COPPER mg/L	IRON mg/L	MERCURY µg/L	MANGANESE mg/L	NICKEL mg/L	LEAD mg/L	ZINC mg/L
373	0.040	-	-	0.0010	-	0.040	-	0.0050	0.003	-	0.0100
373	0.030	-	-	0.0010	-	0.040	-	0.0050	-	-	0.0090
373	-	-	-	-	-	-	-	0.0020	0.003	-	0.0070
375	-	-	-	0.0010	-	-	-	0.0030	0.003	-	0.0080
375	-	-	-	0.0010	-	-	-	0.0030	0.003	-	0.0070
375	-	-	-	0.0010	-	-	-	0.0030	0.003	-	0.0110
374	-	-	-	-	0.0010	-	-	0.0030	-	-	0.0090
374	-	-	-	0.0010	0.0010	-	-	0.0030	0.003	-	0.0100
374	-	-	-	0.0010	0.0010	-	-	0.0030	0.003	-	0.0090
Blank	-	-	-	0.0010	0.0010	-	-	0.0010	-	-	0.0010
Blank	-	-	-	0.0010	-	-	-	-	-	-	-
Blank	-	-	-	0.0010	-	-	-	-	-	-	0.0020
Blank	-	-	-	0.0020	-	-	-	-	-	-	0.0020
Water Quality Objectives		0.1	0.0002	0.1	0.005	0.3	0.2 (filtered)		0.025	0.025	0.03
Method Detection Limit	0.01	0.001	0.0002	0.0005	0.0005	0.02	0.02	0.0005	0.002	0.005	0.0005

" - " = Parameter Was Below the Method Detection Limit

Table A4: Nutrient Concentrations and Physical Parameters of Water Collected From the St. Lawrence River, 1991. All samples were collected from 1 m below the surface. There are three replicates per station.

Station Number	ALKALINITY mg/L	COND25 μMHO/cm	DOC mg/l	TEMP °C	TKN mg/L	PHOSPHORUS mg/L
82	100.9	310	2.2	0.5	0.260	0.011
82	100.3	309	2.1	0.5	0.230	0.023
82	100.4	309	2.2	0.5	0.350	0.070
83	99.5	307	2.2	0.3	0.220	0.010
83	99.6	306	1.9	0.3	0.230	0.009
83	99.4	307	2	0.3	0.210	0.008
365	100.4	311	2.2	0.4	0.230	0.009
365	100.2	311	2.1	0.4	0.230	0.010
365	100.1	310	2.5	0.4	0.250	0.011
366	99.9	308	2.1	0.3	0.280	0.016
366	99.8	308	2.1	0.3	0.280	0.012
366	100	309	2.2	0.3	0.350	0.018
404	100.3	309	2.3	0.3	0.270	0.011
404	99.9	309	2.3	0.3	0.240	0.010
404	100.7	310	2.3	0.3	0.410	0.014
368	98.8	310	2.2	0.4	0.300	0.011
368	99	310	2.6	0.4	0.250	0.011
368	99.2	311	2	0.4	0.200	0.010

Table A4 continued

Station Number	ALKALINITY mg/L	COND25 μ MHO/cm	DOC mg/l	TEMP °C	TKN mg/L	PHOSPHORUS mg/L
368A	98.9	310	2.5	0.4	0.230	0.011
368A	98.9	310	2.2	0.4	0.230	0.010
368A	99.2	311	2.4	0.4	0.260	0.012
369	101.3	312	2.2	0.3	0.270	0.011
369	99.8	311	2.2	0.3	0.240	0.013
369	100.1	312	2.2	0.3	0.280	0.021
369A	100.1	309	2	0.3	0.280	0.011
369A	99.7	309	2.4	0.3	0.260	0.012
369A	100.2	309	2.1	0.3	0.300	0.014
370	99.5	311	2.2	0.4	0.250	0.009
370	99.8	312	2.1	0.4	0.230	0.008
370	99.8	313	2.2	0.4	0.220	0.009
370A	100.2	308	2.1	0.3	0.250	0.011
370A	100	308	2.2	0.3	0.310	0.014
370A	99.9	309	2	0.3	0.240	0.009
371	100.4	335	2.3	0.4	0.240	0.008
371	101.5	334	2.3	0.4	0.250	0.010
371	100.7	334	2.1	0.4	0.250	0.013

Table A4 continued

Station Number	ALKALINITY mg/L	COND25 μ MHO/cm	DOC mg/l	TEMP °C	TKN mg/L	PHOSPHORUS mg/L
372	100.2	304	2	0.4	0.230	0.011
372	99.2	305	2.2	0.4	0.230	0.011
372	98.7	305	2	0.4	0.230	0.010
376	99.1	307	2.1	0.4	0.250	0.011
376	99	307	2.6	0.4	0.250	0.010
376	98.7	307	2.1	0.4	0.260	0.011
373	ND	310	2.5	0.4	0.400	0.032
373	98.6	310	2.2	0.4	0.330	0.025
373	98.8	310	2.1	0.4	0.360	0.028
375	98.7	310	2.1	0.4	0.210	0.008
375	98.9	309	2.2	0.4	0.210	0.007
375	99.3	310	2	0.4	0.220	0.007
374	100.1	312	2.2	0.2	0.250	0.019
374	100.4	313	2.3	0.2	0.350	0.014
374	100.8	313	2.3	0.2	0.310	0.014
Blank	1.6	4	0.4	ND	0.070	0.002
Blank	2	4	0.3	0.4	0.100	0.002 < MDL
Blank	1.9	4	0.2	0.4	0.090	0.002 < MDL
Blank	2	4	0.7	0.4	0.090	0.002

Table A5: Concentration of Metals in Sediment Collected From the St. Lawrence River, 1991. There are two or three replicate samples per station.

Station Number	Sample Depth (m)	Aluminum $\mu\text{g/g}$	Arsenic $\mu\text{g/g}$	Cadmium $\mu\text{g/g}$	Chromium $\mu\text{g/g}$	Copper $\mu\text{g/g}$	Iron $\mu\text{g/g}$	Manganese $\mu\text{g/g}$	Nickel $\mu\text{g/g}$	Lead $\mu\text{g/g}$	Selenium $\mu\text{g/g}$	Zinc $\mu\text{g/g}$
82	2.0	10000	2.70	1.10	25	20	14000	230	18	19	0.59	79
82	2.0	11000	3.00	1.20	26	20	14000	240	18	18	0.64	80
82	2.0	12000	2.60	1.30	27	21	15000	220	21	19	0.71	83
82 (split)	2.0	11000	2.80	1.20	27	21	14000	220	20	18	0.62	83
83	4.0	6000	1.70	0.85	15	11	9400	190	13	15	0.35	53
83	4.0	5900	1.70	0.68	15	10	9400	180	12	9.8	0.31	49
83	4.0	5600	1.90	0.86	14	10	9200	180	12	12	0.37	50
365	1.5	10000	4.30	1.50	36	48	15000	240	28	36	1.40	120
365	1.5	11000	4.40	1.40	30	52	15000	250	24	35	1.50	110
366	1.5	7300	1.40	0.60	18	14	11000	250	13	14	0.53	49
366	1.5	6900	1.90	0.60	16	13	10000	240	12	13	0.56	45
366	1.5	6900	1.70	0.74	17	14	11000	250	13	11	0.52	48
366 (split)	1.5	7400	1.70	0.66	18	17	11000	250	14	13	0.44	52
Lowest Effect Level												
			6	0.6	26	16	2%	460	16	31		120
Severe Effect Level												
			33	10	110	110	4%	1100	76	250		820

Table A5 continued

Station Number	Sample Depth (m)	Aluminum $\mu\text{g/g}$	Arsenic $\mu\text{g/g}$	Cadmium $\mu\text{g/g}$	Chromium $\mu\text{g/g}$	Copper $\mu\text{g/g}$	Iron $\mu\text{g/g}$	Manganese $\mu\text{g/g}$	Nickel $\mu\text{g/g}$	Lead $\mu\text{g/g}$	Selenium $\mu\text{g/g}$	Zinc $\mu\text{g/g}$
404	3.0	5800	1.50	0.73	17	16	10000	200	14	23	0.39	57
404	3.0	5500	1.40	0.80	16	19	9900	190	14	18	0.42	56
404	3.0	5300	1.40	0.75	15	16	9800	200	13	24	0.39	44
368	4.0	13000	3.90	1.60	55	110	16000	240	27	410	2.30	1200
368	4.0	11000	3.80	1.60	53	110	15000	230	26	520	3.00	1300
368	4.0	12000	3.60	1.70	55	100	16000	240	27	410	2.40	1200
368 (split)	4.0	13000	5.00	1.60	51	95	17000	240	29	280	2.10	1200
368A	10.0	12000	3.40	1.40	31	31	15000	280	22	37	1.00	430
368A	10.0	9900	2.80	1.10	24	26	13000	260	18	28	0.87	340
369	3.0	13000	4.10	1.50	34	41	16000	260	24	44	1.50	370
369	3.0	13000	4.30	1.70	36	41	16000	270	25	44	1.60	380
369A	9.5	6400	1.80	1.00	18	22	12000	170	15	34	1.15	130
369A	9.5	6900	1.50	0.79	20	19	12000	180	15	25	1.03	140
369A	9.5	7400	2.20	0.91	21	25	12000	180	17	34	1.12	160
369A (split)	9.5	7300	1.80	1.00	20	21	12000	180	17	33	1.15	160
Lowest Effect Level			6	0.6	26	16	2%	460	16	31		120
Severe Effect Level			33	10	110	110	4%	1100	75	250		820

Table A5 continued

Station Number	Sample Depth (m)	Aluminum $\mu\text{g/g}$	Arsenic $\mu\text{g/g}$	Cadmium $\mu\text{g/g}$	Chromium $\mu\text{g/g}$	Copper $\mu\text{g/g}$	Iron $\mu\text{g/g}$	Manganese $\mu\text{g/g}$	Nickel $\mu\text{g/g}$	Lead $\mu\text{g/g}$	Selenium $\mu\text{g/g}$	Zinc $\mu\text{g/g}$
370	2.5	15000	5.90	1.60	37	43	17000	320	28	36	2.10	630
370	2.5	15000	5.10	1.50	36	42	16000	330	29	38	1.80	620
370	2.5	15000	5.30	1.80	36	44	16000	310	27	34	2.00	600
370A	10.0	3900	0.87	0.59	15	9.9	6700	150	12	11	0.42	69
370A	10.0	3800	0.87	0.50	10	8.8	6600	150	9.8	11	0.42	63
370A	10.0	3900	0.91	0.39	11	12	6700	140	10	10	0.38	64
371	6.0	16000	5.50	2.30	40	61	19000	310	30	41	2.10	620
371	6.0	16000	6.20	2.20	40	59	19000	300	30	41	2.00	610
372	6.0	8600	2.10	0.61	20	17	13000	240	16	13	0.65	59
372	6.0	8900	1.70	0.93	21	17	13000	240	17	14	0.72	62
376	4.5	15000	6.30	1.70	41	46	17000	280	30	40	2.70	560
376	4.5	15000	6.60	1.70	42	47	17000	290	31	39	2.80	560
Lowest Effect Level			6	0.6	26	16	2%	460	16	31		120
Severe Effect Level			33	10	110	110	4%	1100	75	250		820

Table A5 continued

Station Number	Sample Depth (m)	Aluminum $\mu\text{g/g}$	Arsenic $\mu\text{g/g}$	Cadmium $\mu\text{g/g}$	Chromium $\mu\text{g/g}$	Copper $\mu\text{g/g}$	Iron $\mu\text{g/g}$	Manganese $\mu\text{g/g}$	Nickel $\mu\text{g/g}$	Lead $\mu\text{g/g}$	Selenium $\mu\text{g/g}$	Zinc $\mu\text{g/g}$
373	1.5	7700	1.30	0.60	16	8.8	11000	170	11	9.5	0.32	74
373	1.5	7300	1.10	0.36	16	8.6	10000	160	11	8.4	0.29	76
375	4.0	20000	5.30	2.10	51	58	21000	290	36	57	2.20	460
375	4.0	19000	5.90	2.00	49	55	21000	290	36	49	2.10	450
375	4.0	19000	5.30	2.00	50	56	21000	290	35	55	2.10	460
375 (split)	4.0	18000	6.40	2.20	54	61	21000	300	37	65	1.90	520
374	13.0	19000	6.70	2.20	48	52	21000	300	37	53	2.59	400
374	13.0	18000	6.90	1.90	47	51	21000	290	35	46	2.59	410
Lowest Effect Level			6	0.6	26	16	2%	460	16	31		120
Severe Effect Level			33	10	110	110	4%	1100	75	250		820

"split" samples refer to a duplicate sample and analysis of the previous sample listed to test laboratory precision.

Table A6. Concentrations of Mercury and Methyl Mercury in Sediment Collected From the St. Lawrence River, 1991. There are two or three replicates per station.

Station Number	Total Mercury		Methyl Mercury		
	Dry Weight ($\mu\text{g/g}$)	Wet Weight ($\mu\text{g/g}$)	Dry Weight ($\mu\text{g/g}$)	Wet Weight ($\mu\text{g/g}$)	
82	0.126	0.064	0.0018	0.0009	1.43
82	0.123	0.063	0.0009	0.0005	0.73
82	0.115	0.059	0.0013	0.0007	1.14
83	0.09	0.052	0.0016	0.0009	1.82
83	0.096	0.056	0.0007	0.0004	0.73
83	0.098	0.056	0.0007	0.0004	0.71
365	3.586	1.259	0.0112	0.0039	0.31
365	2.936	1.139	0.0127	0.0049	0.43
366	0.124	0.045	0.0029	0.0011	2.34
366	0.131	0.045	0.0023	0.0008	1.76
366	0.155	0.057	0.00125	0.00045	0.81
404	0.599	0.162	0.0065	0.0018	1.09
404	0.538	0.153	0.007	0.002	1.31
404	0.544	0.14	0.0086	0.0022	1.58
368	3.089	1.662	0.0073	0.0039	0.24
368	2.995	1.605	0.0061	0.0033	0.2
368	3.295	1.5605	0.00925	0.00435	0.28
368A	2.276	0.983	0.0078	0.0034	0.34
368A	2.916	1.091	0.009	0.0034	0.31
369	3.172	1.481	0.0071	0.0033	0.22
369	3.404	1.559	0.0112	0.0051	0.33
369A	1.091	0.309	0.0089	0.0025	0.82
369A	0.861	0.234	0.0072	0.002	0.84
369A	0.983	0.293	0.00845	0.0025	0.86
370	0.943	0.223	0.007	0.0017	0.74
370	0.867	0.218	0.0019	0.0005	0.22
370	1.228	0.296	0.0042	0.001	0.34
370A	1.103	0.483	0.0104	0.0046	0.94

370A	1.103	0.48	0.0064	0.0028	0.58
370A	1.321	0.555	0.0101	0.0042	0.76
371	0.999	0.3	0.0156	0.0047	1.56
371	1.195	0.355	0.0051	0.0015	0.43
372	0.165	0.046	0.004	0.0011	2.42
372	0.159	0.045	0.0038	0.0011	2.39
376	1.159	0.306	0.0021	0.0006	0.18
376	1.203	0.306	0.0029	0.0008	0.25
373	0.064	0.04	0.001	0.0006	1.56
373	0.048	0.03	0.0009	0.0006	1.88
375	1.046	0.633	0.0019	0.0011	0.18
375	1.25	0.75	0.0034	0.002	0.27
375	1.188	0.714	0.00245	0.00145	0.21
374	0.293	0.195	0.0011	0.0007	0.38
374	0.218	0.145	0.0042	0.0028	1.93

Table A7. The Ratio of Lead, Zinc, Copper and Mercury Concentrations in the Sediment to Sediment Aluminum Concentrations.

Station Number	Lead	Zinc	Copper	Mercury
82	0.002	0.007	0.002	$1.1 \cdot 10^{-5}$
83	0.002	0.009	0.002	$1.5 \cdot 10^{-5}$
365	0.003	0.011	0.005	$3.1 \cdot 10^{-4}$
366	0.002	0.0067	0.001	$1.96 \cdot 10^{-5}$
404	0.004	0.009	0.003	$1.0 \cdot 10^{-4}$
368	0.03	0.10	0.009	$2.57 \cdot 10^{-4}$
368A	0.003	0.035	0.003	$2.37 \cdot 10^{-4}$
369	0.003	0.029	0.003	$2.53 \cdot 10^{-4}$
369A	0.004	0.021	0.003	$1.42 \cdot 10^{-4}$
370	0.002	0.04	0.003	$6.73 \cdot 10^{-5}$
370A	0.003	0.017	0.003	$3.02 \cdot 10^{-4}$
371	0.003	0.038	0.004	$6.87 \cdot 10^{-5}$
372	0.001	0.007	0.002	$1.8 \cdot 10^{-5}$
376	0.003	0.037	0.003	$7.87 \cdot 10^{-5}$
373	0.001	0.01	0.001	$8 \cdot 10^{-6}$
375	0.003	0.024	0.003	$6.05 \cdot 10^{-5}$
374	0.003	0.022	0.003	$1.4 \cdot 10^{-5}$

Table A8: Concentration of Nutrients and Physical Parameters in Sediment Collected From the St. Lawrence River, 1991. There are two or three replicates per station.

Station Number	Sample Depth (m)	TKN mg/g	PHOSPHORUS mg/g	SULPHUR %	LOI mg/g	TOC mg/g	SUM 1 Clay %	SUM 2 Silt %	SUM 3 Sand %
82	2.0	2.40	0.93	0.097	49.0	25.00	4.69	56.70	36.70
82	2.0	2.50	1.00	0.120	50.0	28.00	5.85	57.90	34.20
82	2.0	2.90	1.00	0.130	55.0	30.00	4.67	60.40	33.80
82 (split)	2.0	2.60	0.90	0.100	54.0	27.00	4.64	58.60	35.40
83	4.0	1.20	0.88	0.055	20.0	9.80	1.93	29.20	68.40
83	4.0	1.10	0.83	0.053	19.0	10.00	2.03	30.20	67.20
83	4.0	1.00	0.83	0.049	19.0	12.00	2.22	28.00	69.50
365	1.5	4.30	0.85	0.510	120.0	75.00	4.59	55.40	35.10
365	1.5	4.60	0.88	0.470	110.0	76.00	5.61	56.10	34.00
366	1.5	1.80	0.70	0.123	33.0	19.00	3.76	31.50	60.20
366	1.5	1.80	0.75	0.120	32.0	14.00	4.56	31.30	58.90
366	1.5	1.80	0.77	0.134	31.0	16.00	3.79	31.90	58.90
366 (split)	1.5	2.00	0.93	0.122	31.0	15.00	4.17	31.20	59.10
404	3.0	1.40	0.74	0.160	27.0	16.00	1.92	23.10	69.80
404	3.0	1.30	0.68	0.160	25.0	15.00	2.09	21.10	70.40
404	3.0	1.20	0.65	0.160	24.0	15.00	2.01	20.30	71.50
Lowest Effect Level		0.55	0.6			1%			
Severe Effect Level		4.8	2.0			10%			

Table A8 continued

Station Number	Sample Depth (m)	TKN mg/g	PHOSPHORUS mg/g	SULPHUR %	LOI mg/g	TOC mg/g	SUM 1 Clay %	SUM 2 Silt %	SUM 3 Sand %
368	4.0	3.00	1.00	0.750	68.0	36.00	9.80	70.20	19.00
368	4.0	2.70	0.94	0.590	62.0	32.00	10.10	72.30	16.80
368	4.0	2.90	0.94	0.800	67.0	38.00	8.55	70.60	19.90
368 (split)	4.0	3.80	1.00	0.610	71.0	38.00	1.93	80.10	17.20
368A	10.0	2.90	0.97	0.210	49.0	28.00	1.97	17.80	73.80
368A	10.0	2.20	0.84	0.190	39.0	24.00	3.73	27.90	48.20
369	3.0	4.20	1.30	0.400	75.0	37.00	8.61	67.20	20.20
369	3.0	4.10	1.10	0.350	77.0	39.00	8.59	66.30	20.80
369A	9.5	2.10	0.96	0.190	33.0	22.00	3.99	31.70	62.90
369A	9.5	2.00	0.88	0.220	34.0	20.00	3.51	31.20	63.60
369A	9.5	2.20	0.84	0.230	50.0	27.00	3.74	33.60	61.10
369A (split)	9.5	2.10	0.81	0.270	49.0	30.00	4.09	36.80	57.30
370	2.5	7.90	1.10	0.480	110.0	53.00	10.30	67.50	18.20
370	2.5	7.90	1.30	0.450	99.0	52.00	12.60	64.10	17.50
370	2.5	7.00	1.20	0.480	100.0	52.00	10.40	66.60	18.80
Lowest Effect Level		0.55	0.6			1%			
Severe Effect Level		4.8	2.0			10%			

Table A8 continued

Station Number	Sample Depth (m)	TKN mg/g	PHOSPHORUS mg/g	SULPHUR %	LOI mg/g	TOC mg/g	SUM 1 Clay %	SUM 2 Silt %	SUM 3 Sand %
370A	10.0	0.87	0.55	0.110	25.0	14.00	1.89	14.50	74.50
370A	10.0	1.10	0.61	0.110	25.0	15.00	1.92	14.90	76.70
370A	10.0	0.96	0.62	0.094	23.0	13.00	1.84	13.30	81.30
371	6.0	6.20	1.20	0.470	97.0	61.00	13.60	75.50	9.46
371	6.0	6.20	1.20	0.480	96.0	50.00	12.90	75.80	9.81
372	6.0	2.80	0.95	0.160	38.0	19.00	5.30	40.10	53.40
372	6.0	2.70	0.81	0.190	38.0	19.00	5.84	40.30	52.80
376	4.5	6.90	1.20	0.520	110.0	61.00	8.36	81.30	9.00
376	4.5	7.60	1.30	0.550	110.0	59.00	11.70	79.10	7.72
373	1.5	1.30	0.99	0.058	24.0	13.00	4.37	29.00	65.30
373	1.5	1.40	1.00	0.051	23.0	12.00	3.38	26.70	68.30
375	4.0	5.70	1.20	0.410	92.0	50.00	ND	ND	ND
375	4.0	6.20	1.40	0.480	98.0	51.00	ND	ND	ND
375	4.0	6.00	1.50	0.430	94.0	49.00	13.00	79.90	6.38
375 (split)	4.0	5.40	1.30	0.390	92.0	47.00	13.20	79.80	6.32
374	13.0	6.90	1.20	0.590	110.0	55.00	13.40	76.70	8.83
374	13.0	6.40	1.10	0.550	120.0	58.00	12.70	78.90	7.53
Lowest Effect Level		0.55	0.6			1%			
Severe Effect Level		4.8	2.0			10%			

"split" samples refer to a duplicate sample and analysis of the previous sample listed.

